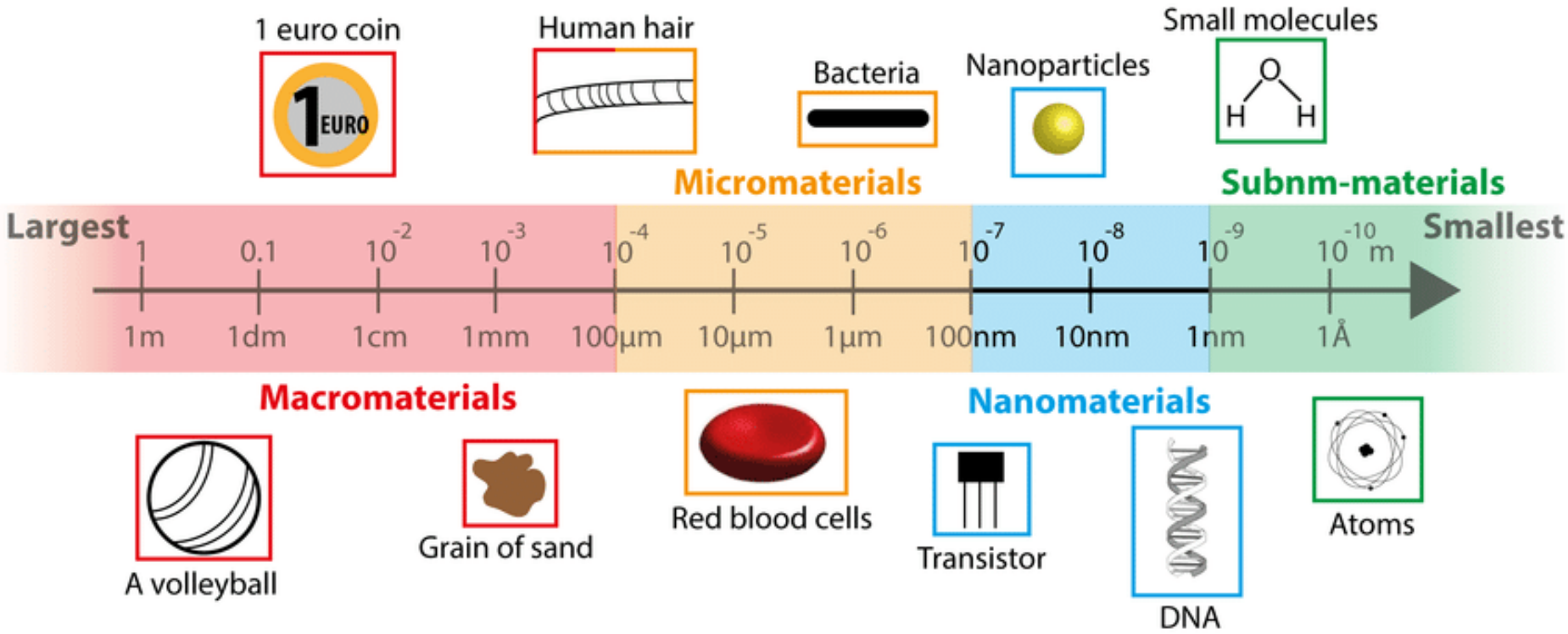
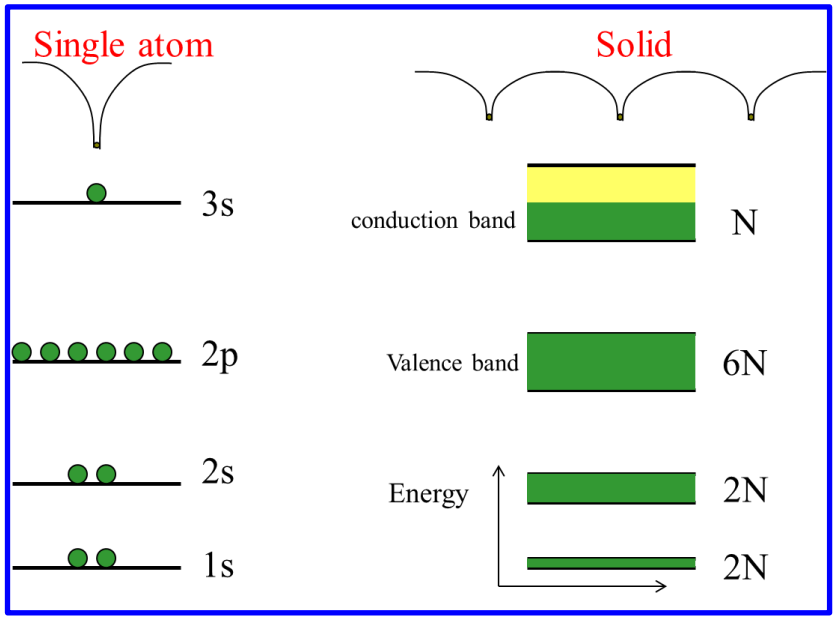
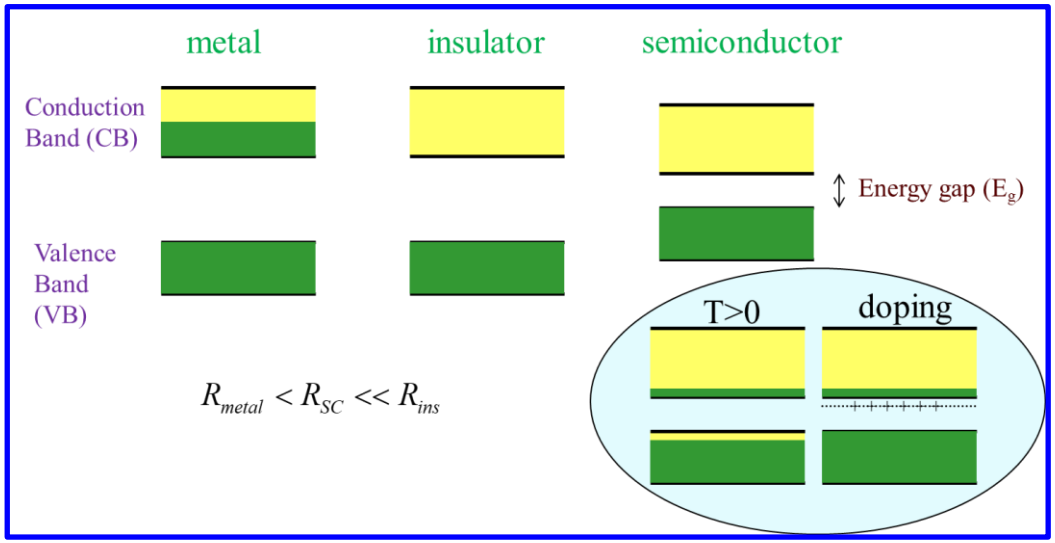
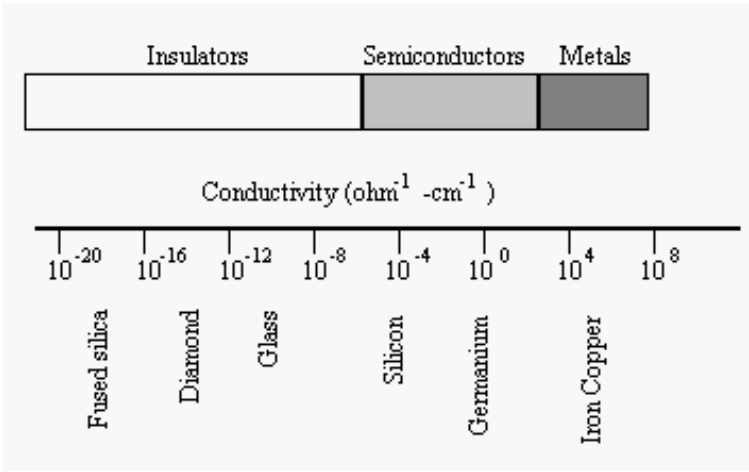
Sizes of different materials

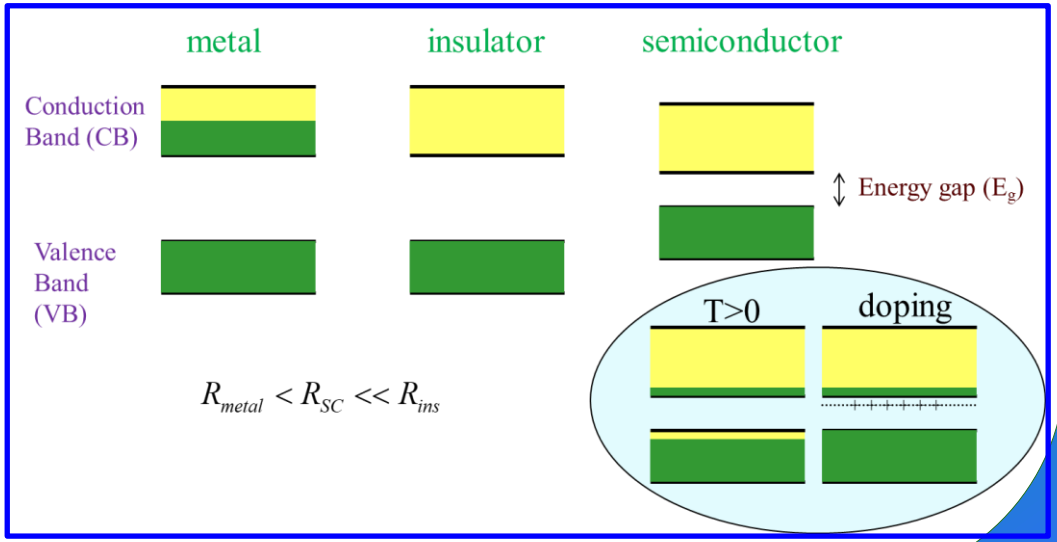


Band diagram of solids



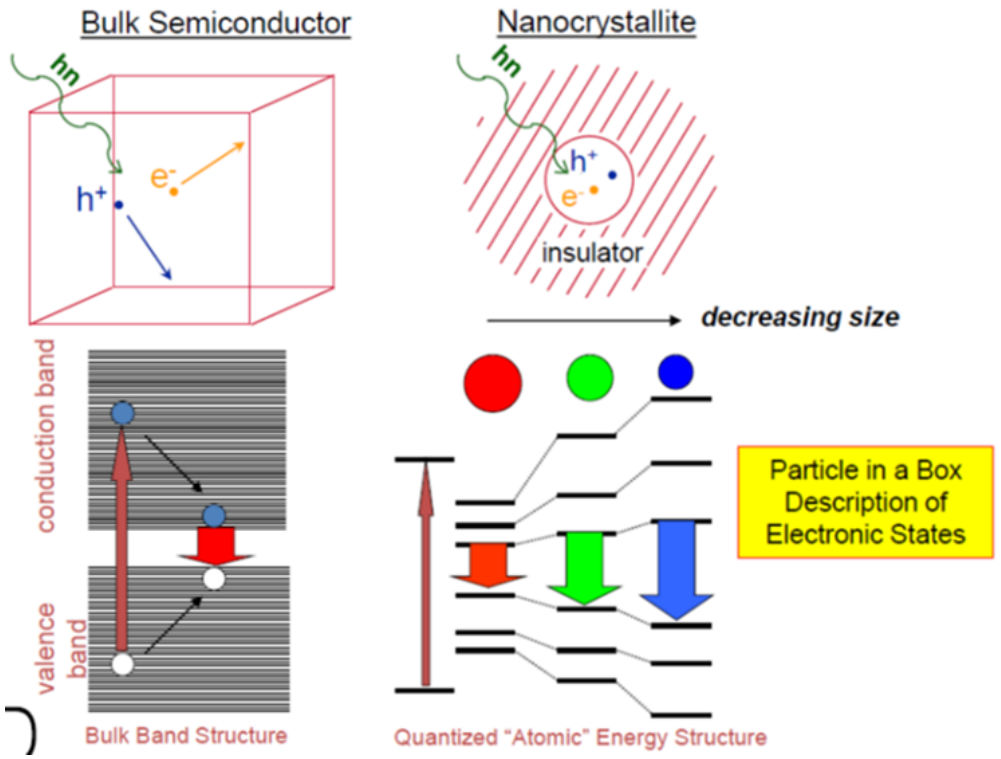






Quantum confinement

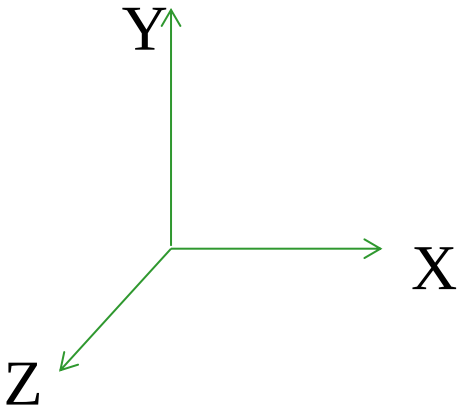
- In a **quantum dot**, relatively few atoms are present and the excitons are confined in the order of the material's exciton Bohr radius. This leads to discrete **quantized energy levels**. For this reason quantum dots have sometimes been referred to as "**artificial atoms**."
- Small changes to the size or composition of a quantum dot allow the energy levels, and the bandgap, to be **fine-tuned** to specific, desired energies.



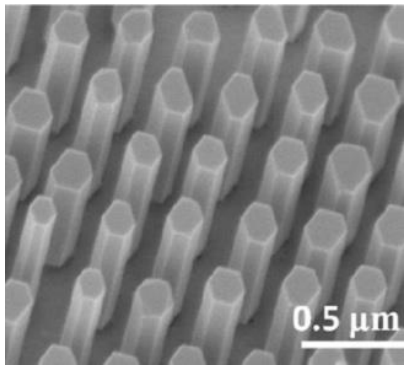
Nanomaterials based on electron confinement

1-D Confined structures

Thin films

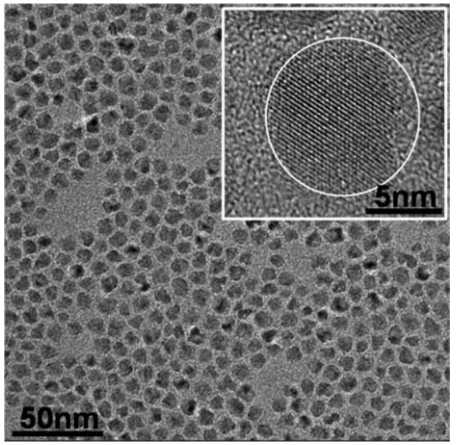


2-D Confined structures



Nanorods

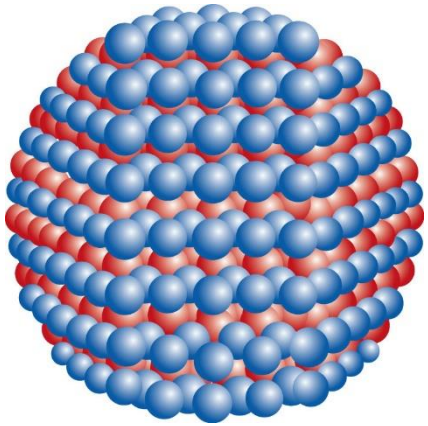
3-D Confined structures



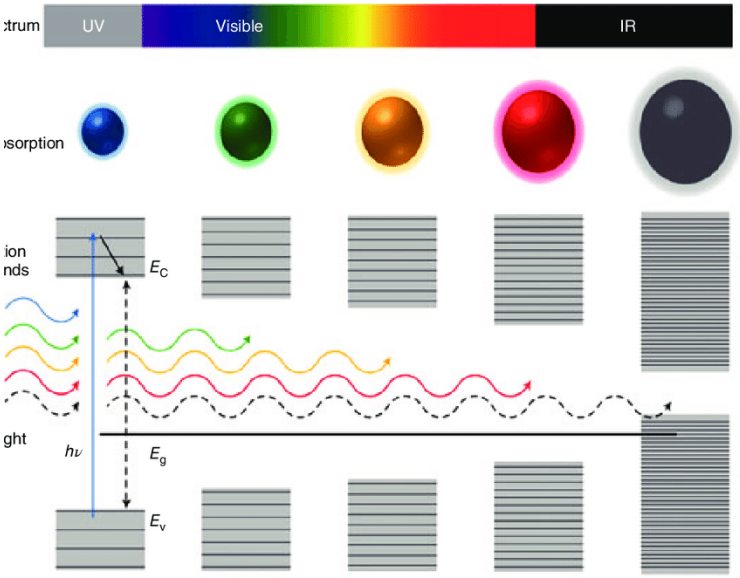
QDs

Quantum dots (QDs): introduction

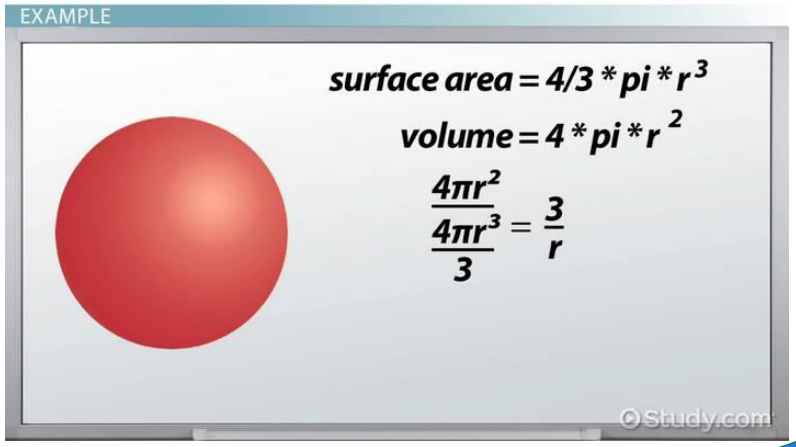
- QDs are semiconductor nanocrystals.
- They are made of many of the same materials as ordinary semiconductors (mainly combinations of transition metals and/or metalloids).
- QDs are extremely small, on the order of a few nanometers. They are very nearly **zero-dimensional**.
- QDs can be less than 10 nanometers (depends on **Exciton Bohr Radius** of the semiconductor), corresponding to 10 to 50 atoms in diameter and a total of 100 to 100,000 atoms within the quantum dot volume.



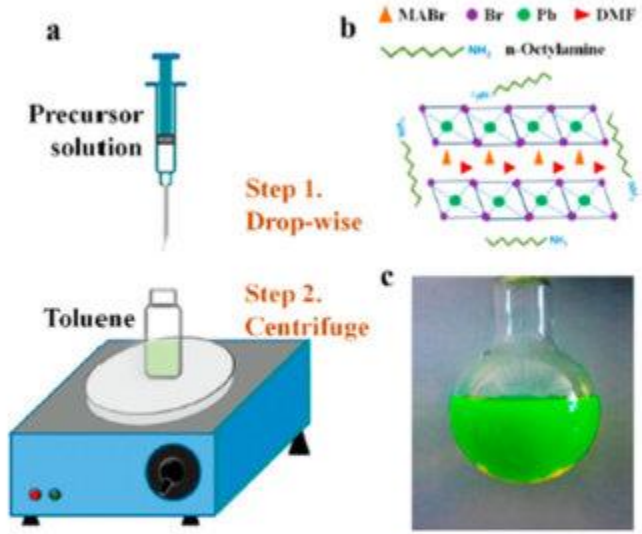
Why QDs are better that their bulk counterpart



- Broad absorption band,
- Narrow emission band,
- Size-tunable emission from visible to near infrared (NIR) spectral range,
- Superior brightness or high photoluminescence quantum yield,
- High color purity,
- Long fluorescent lifetime,



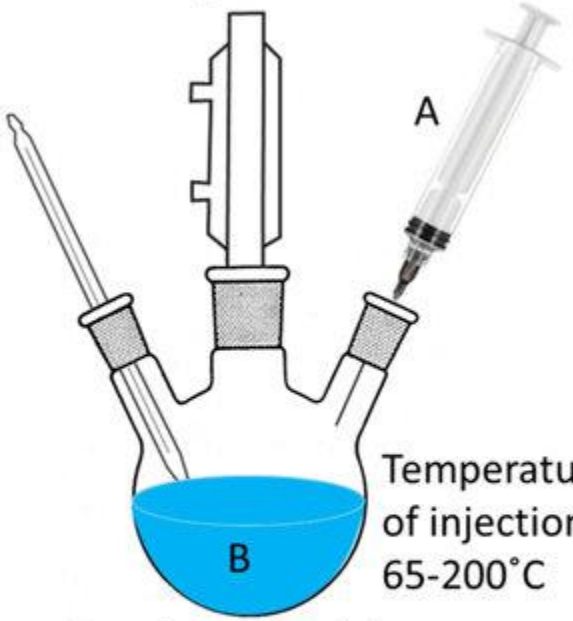
Ligand assisted reprecipitation (LARP)



Precursor solution:
PbX_2 + MAX + capping ligands in DMF

Bad Solvent: Toluene

Hot injection



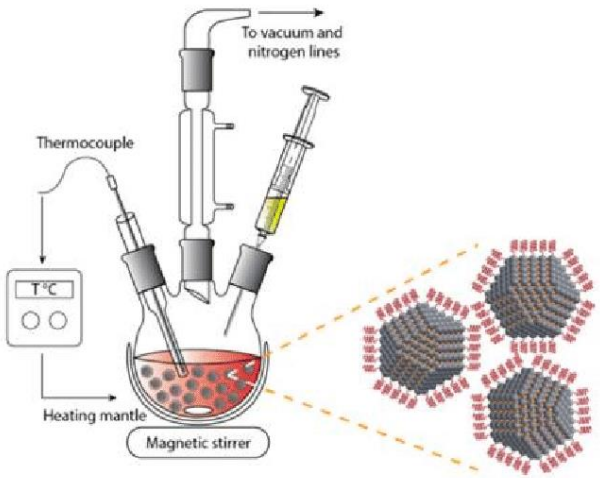
Temperature of injection: 65-200˚C

A: A cation-oleate / Halide precursor

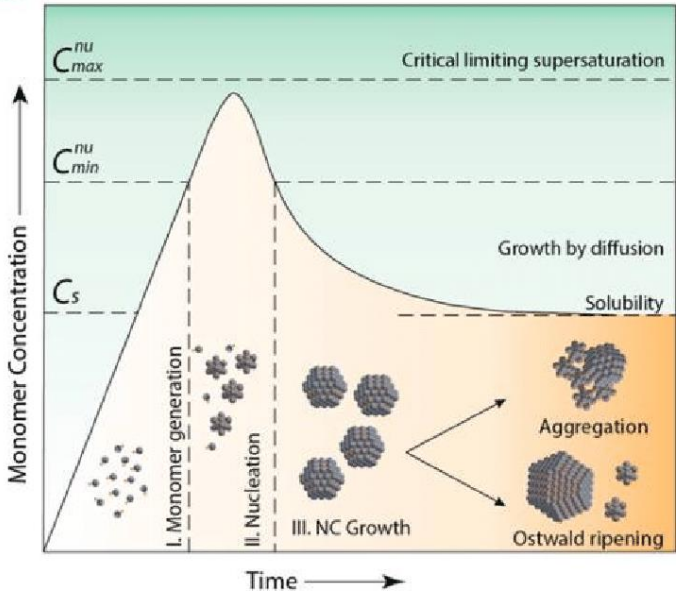
B: PbX_2 in ODE with ligands /Solution of A cations and Pb^{2+} with ligands

Colloidal growth of nanocrystals

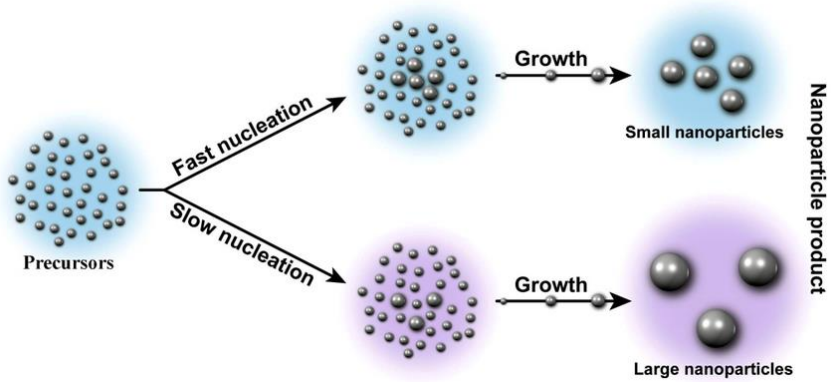
a



b

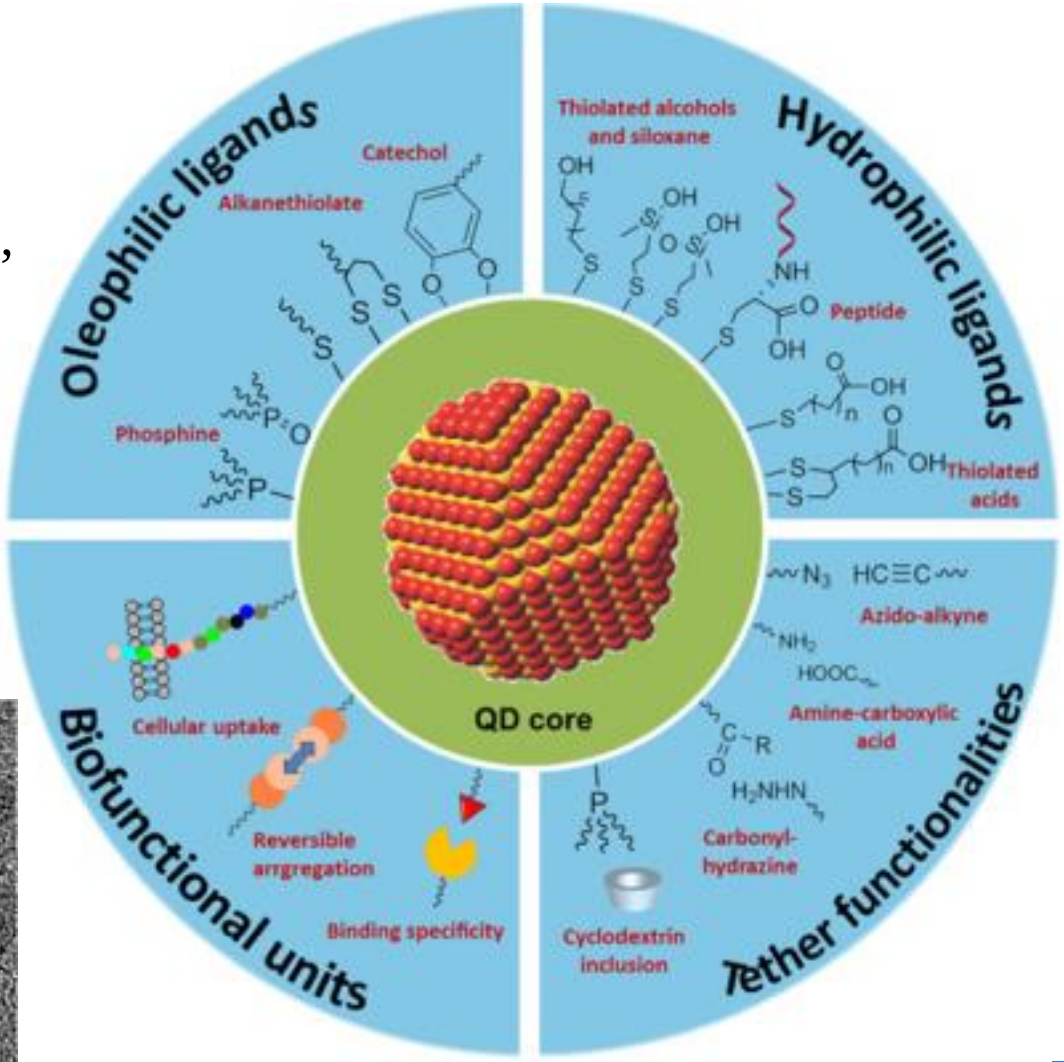


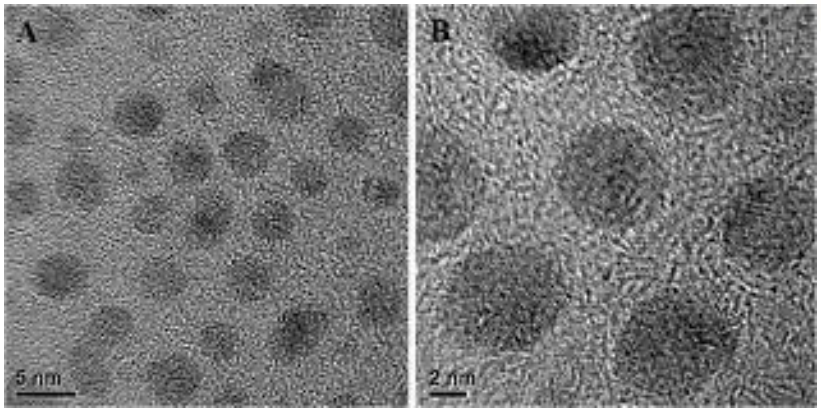
The principle for colloidal synthesis of semiconductor nanocrystals is based on a temporally short cluster nucleation event followed by controlled slow growth on the existing nuclei results in the formation of monodispersed colloids.



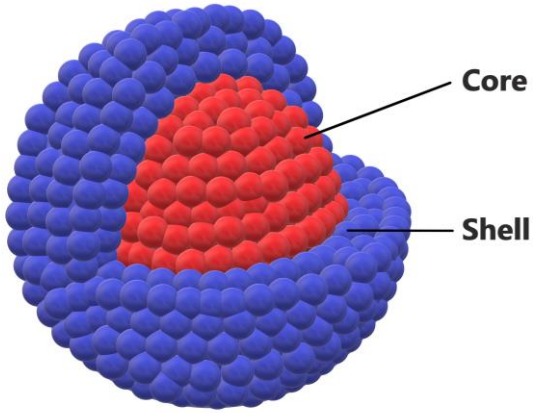
Ligands

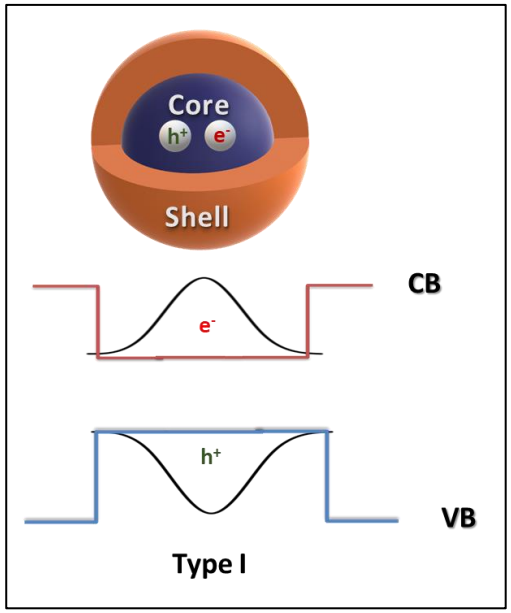
1. Stabilize the QDs,
2. Maintain the size and shape,
3. Determine the solubility,
4. Determine chemical properties,

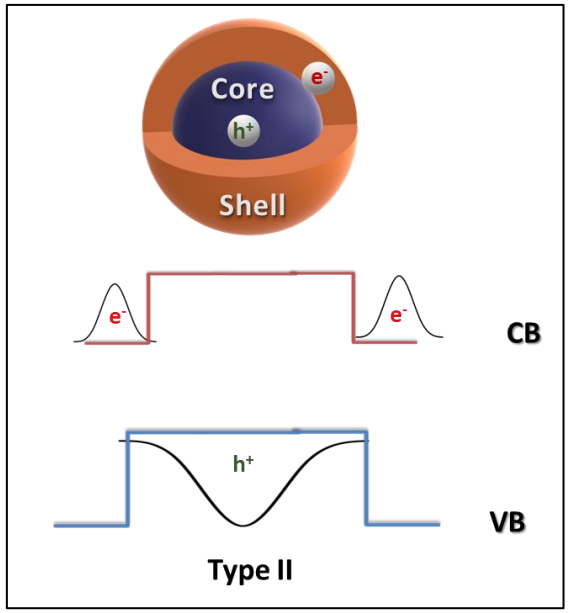




Core-shell nanocrystals





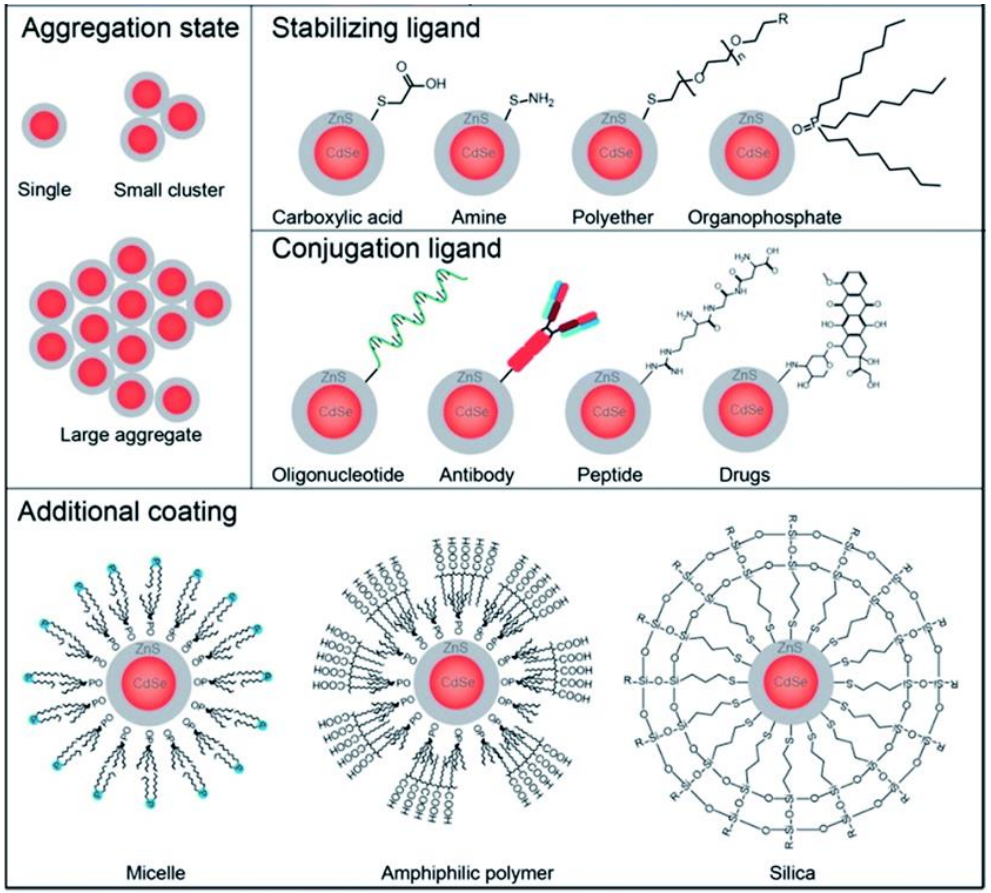


Type-1: Improve PL intensity and stability.

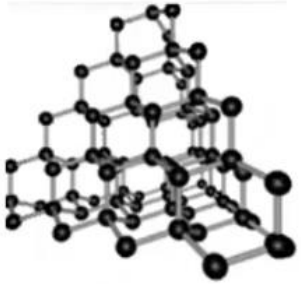
Type-2: Increase charge separation.

Shelling of nanocrystals

- Nanocrystals tend to agglomerate among themselves.
- Synthesis of type-I Nanocrystals, that have higher stability and PL intensity.
- Use of different types of bio-compatible polymers.
- Can coat with bio-molecules, like, proteins, lipids, etc., at the outer most shell of the quantum dots for biocompatibility.

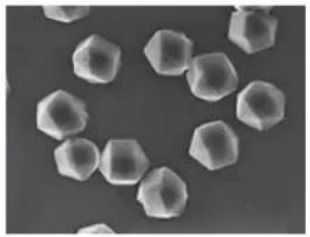


Structure of various carbon nanomaterials

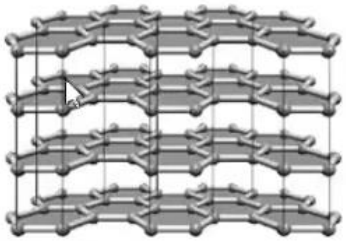


Diamond

Nanocutting

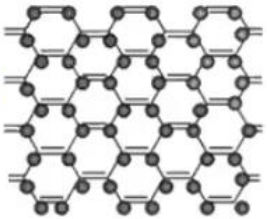


Nanodiamond



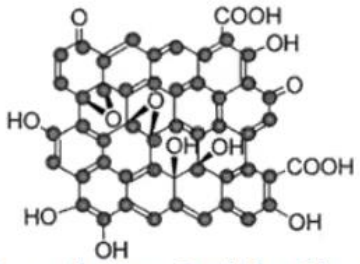
Graphite

Destacking



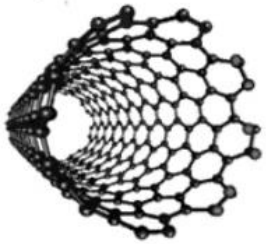
Graphene Sheet

Oxidation



Graphene Oxide Sheet

Folding



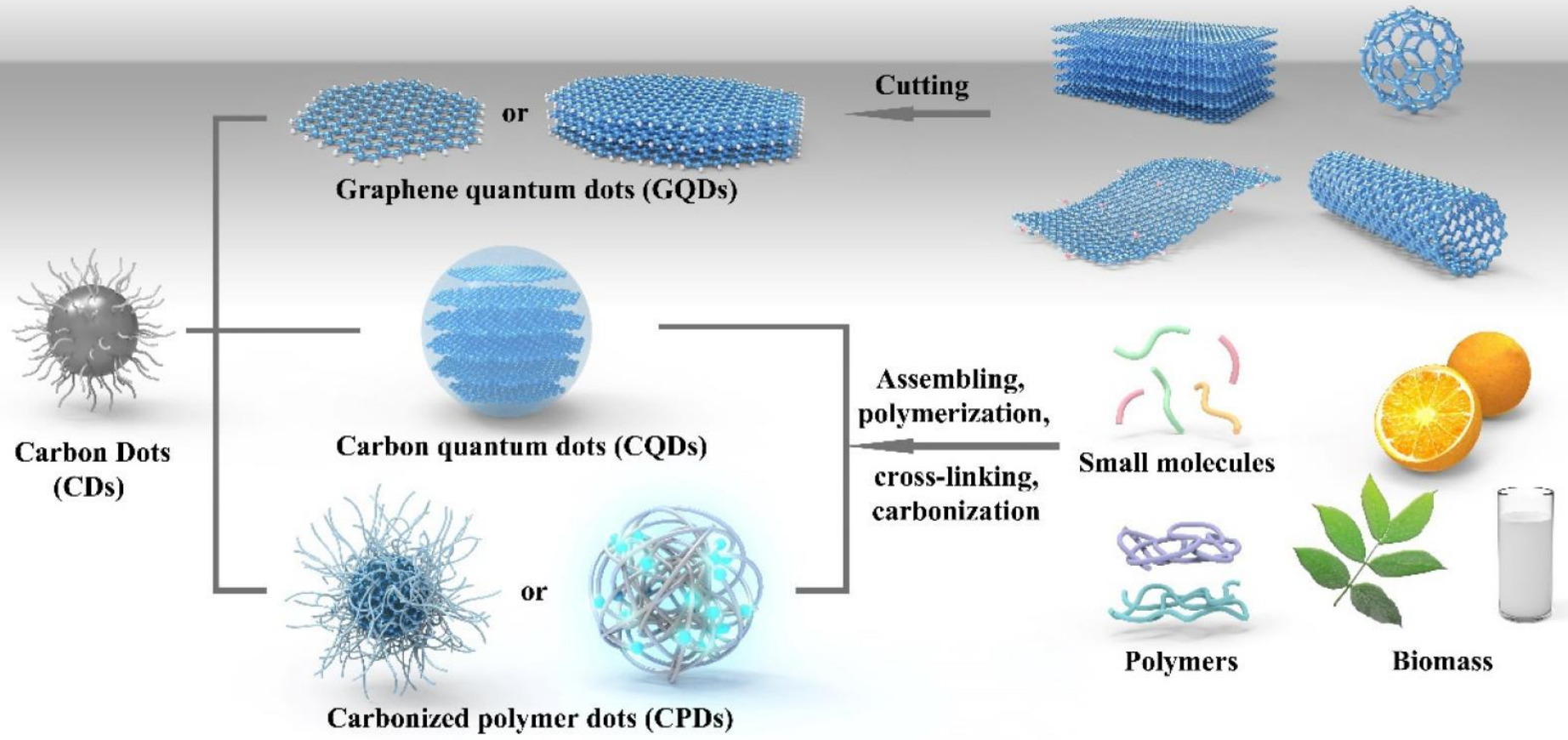
Carbon Nanotube

Nanocutting

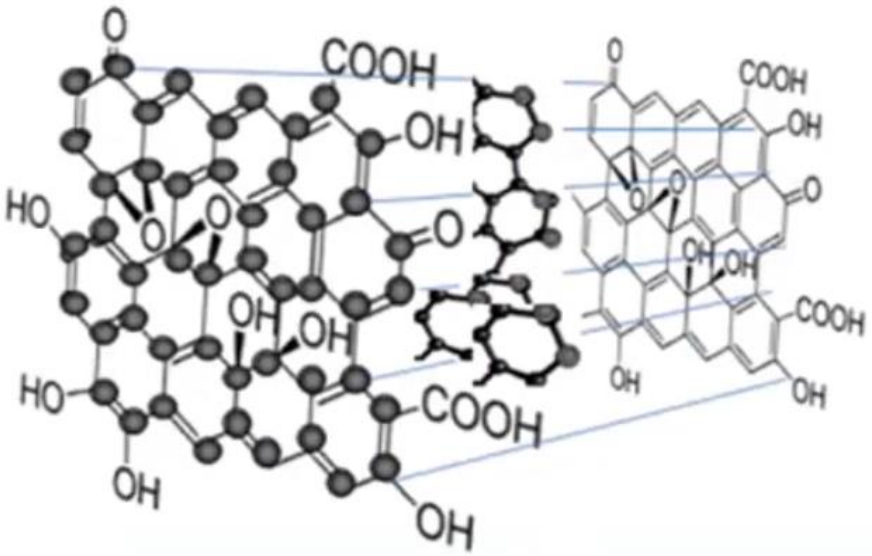
Graphene Quantum Dots

Nanocutting

Graphene Oxide Quantum Dots


Cutting
or
Graphene quantum dots (GQDs)
Carbon Dots
(CDs)
Carbon quantum dots (CQDs)
Assembling,
polymerization,
cross-linking,
carbonization
Small molecules
or
Carbonized polymer dots (CPDs)
Polymers
Biomass

Structure of Carbon Dots!



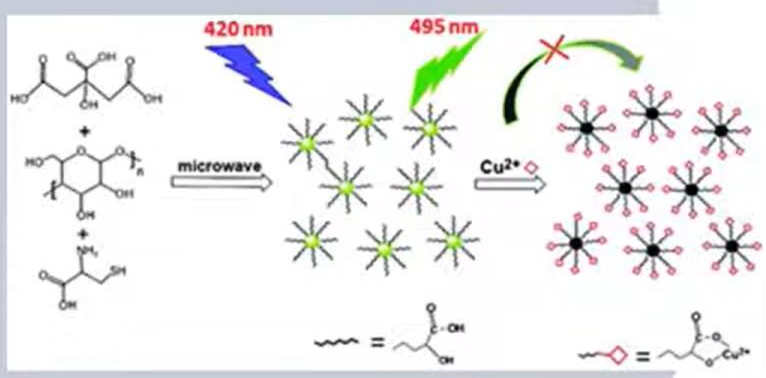
Carbon dots are composed of graphene and graphene oxide sheets fused by diamond-like insertions and containing amorphous structural elements.

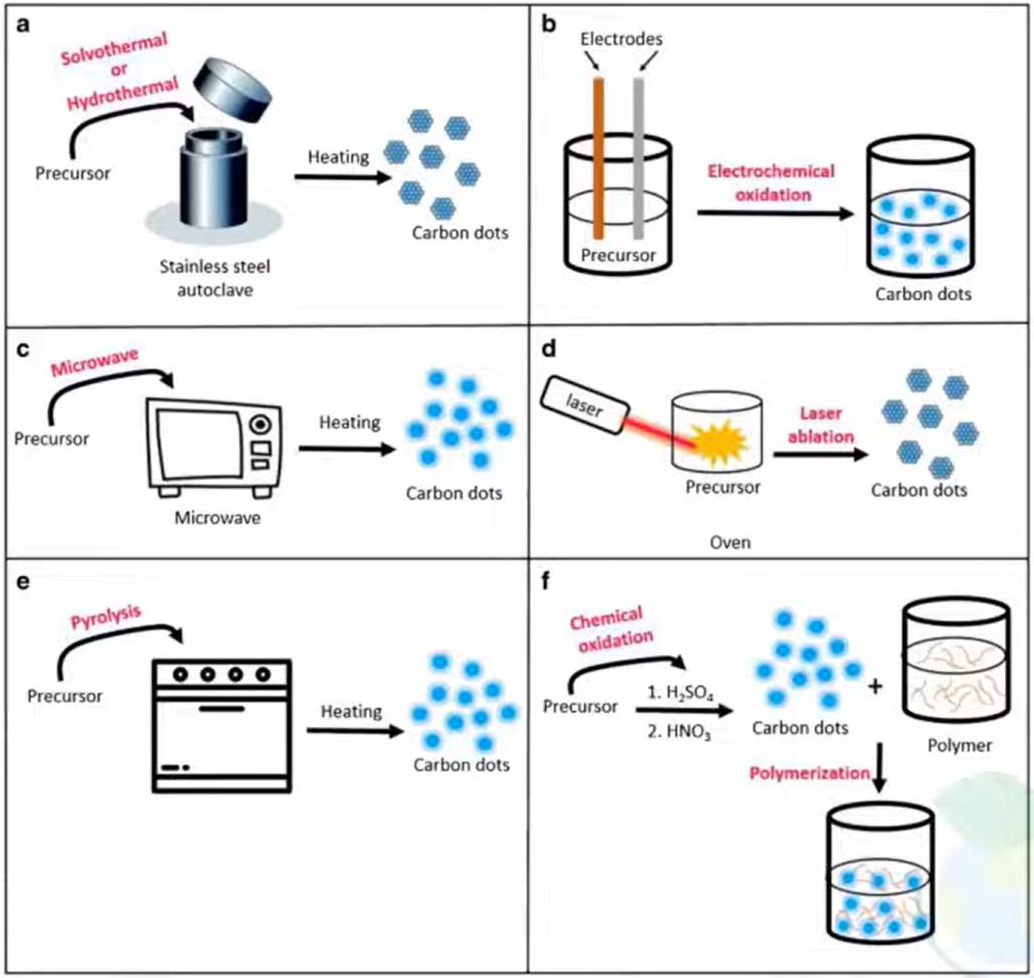
Tentative Definition of Carbon Dots

Based on the data reported in the literature, the CDs can be viewed as a highly defected composition of coexisting aromatic and aliphatic regions, the elementary constituents of which are graphene, graphene oxide and diamond that are assembled in proportions and with variations of surface groups that depend on the conditions of their synthesis.

Demchenko et al., *Methods Appl. Fluoresc.* 1 (2013) 042001

Synthesis of Carbon Dots

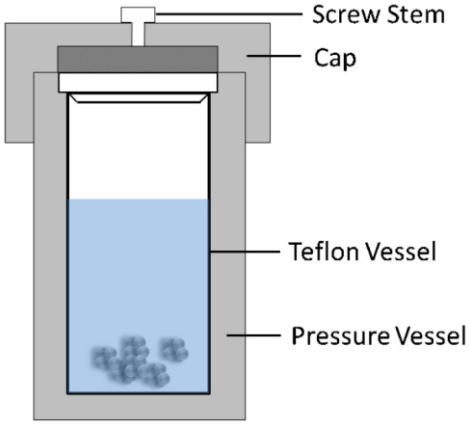


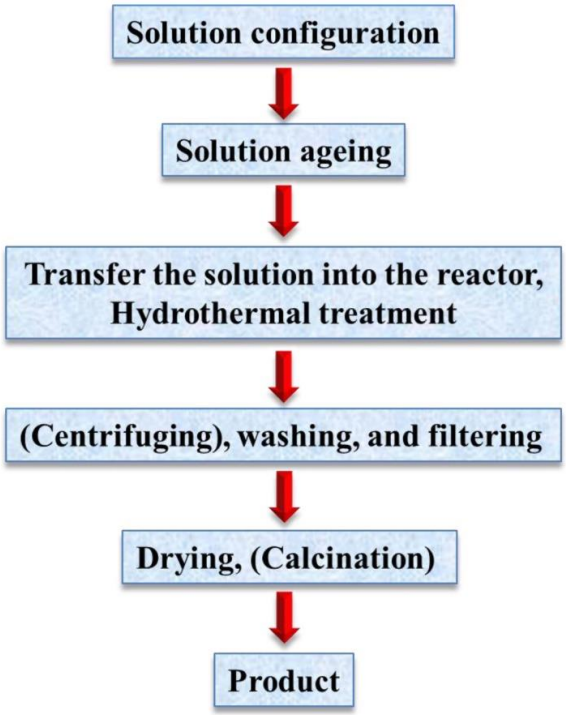


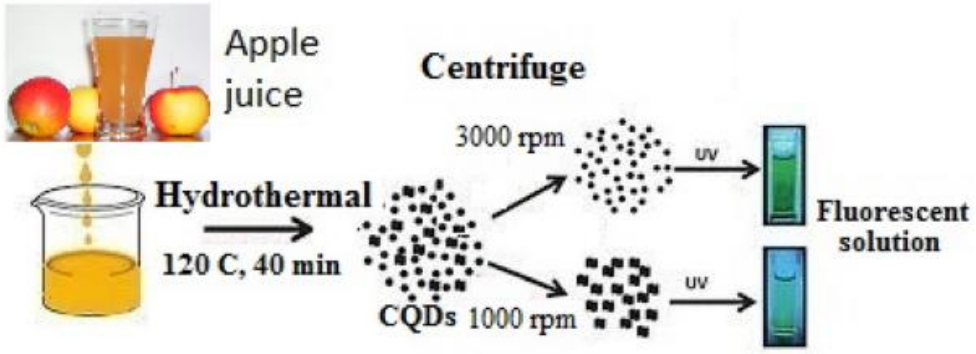
Adapted and Credits to https://link.springer.com/article/10.1007/s00604-019-4091-4

Hydrothermal Method for synthesis of nanocrystals

The hydrothermal method refers to the use of an aqueous solution as a reaction system in a special closed reaction vessel to create a high-temperature, high-pressure reaction environment by heating the reaction system and pressurizing it.

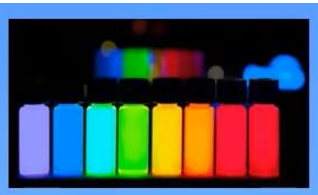




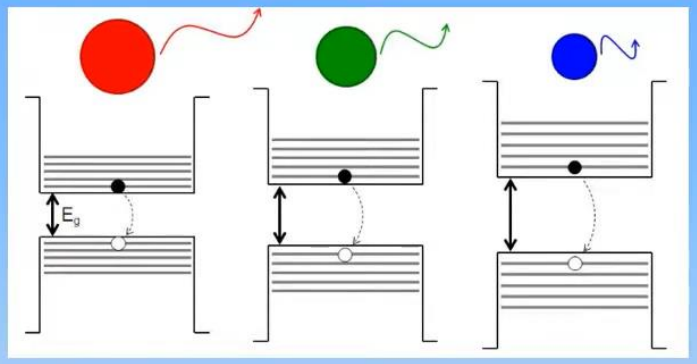


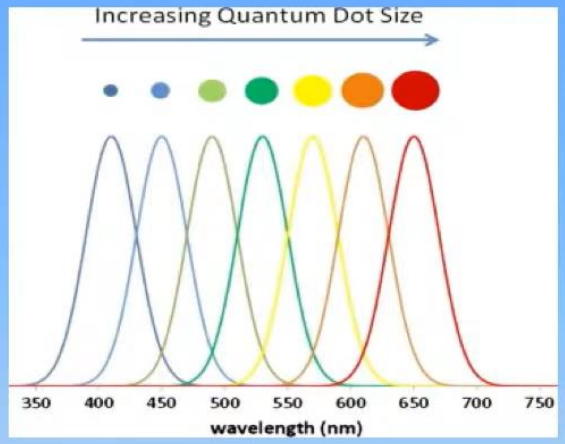
Nitrogen doped carbon dots

Why different colors?

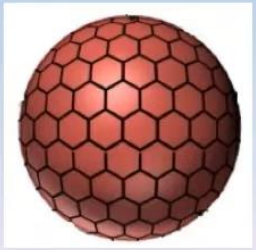


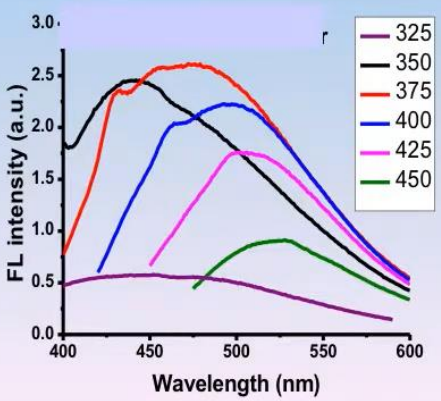
Semiconductor quantum dots:

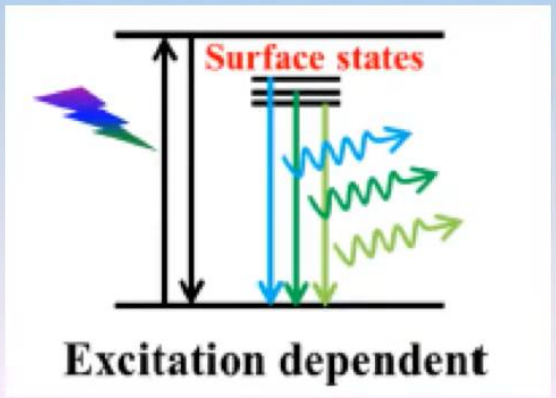




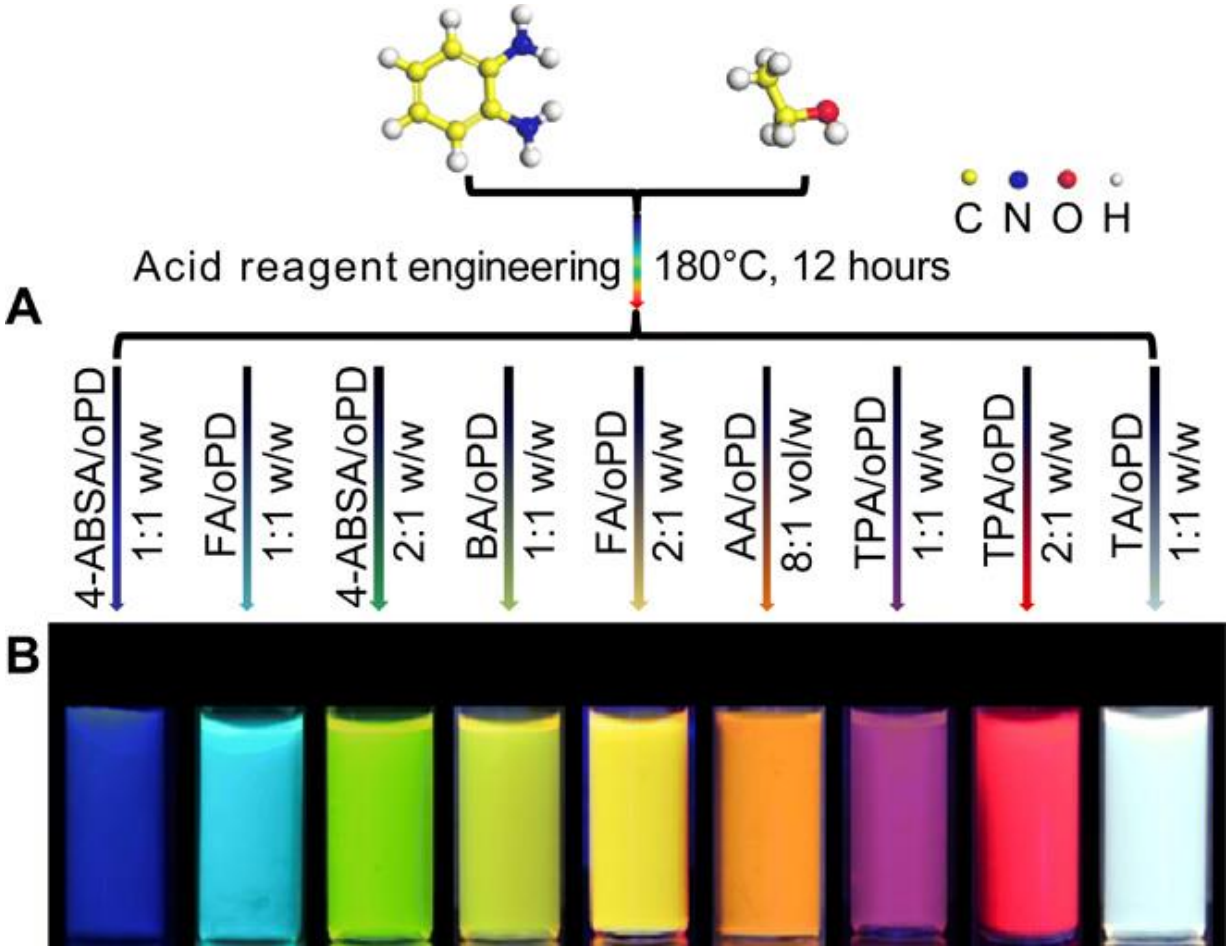
Carbon dots:







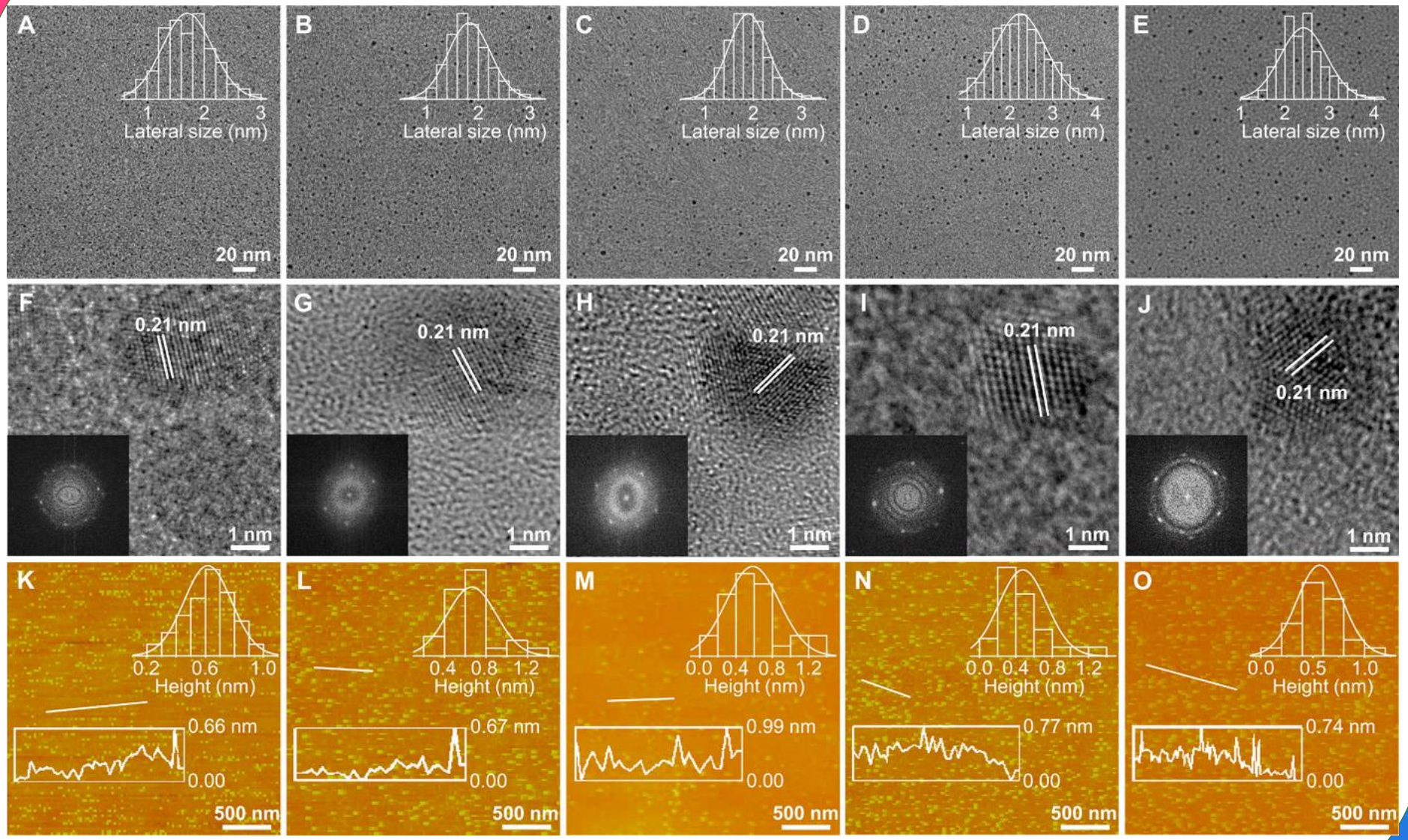
Hydrothermal synthesis of color tunable CQDs

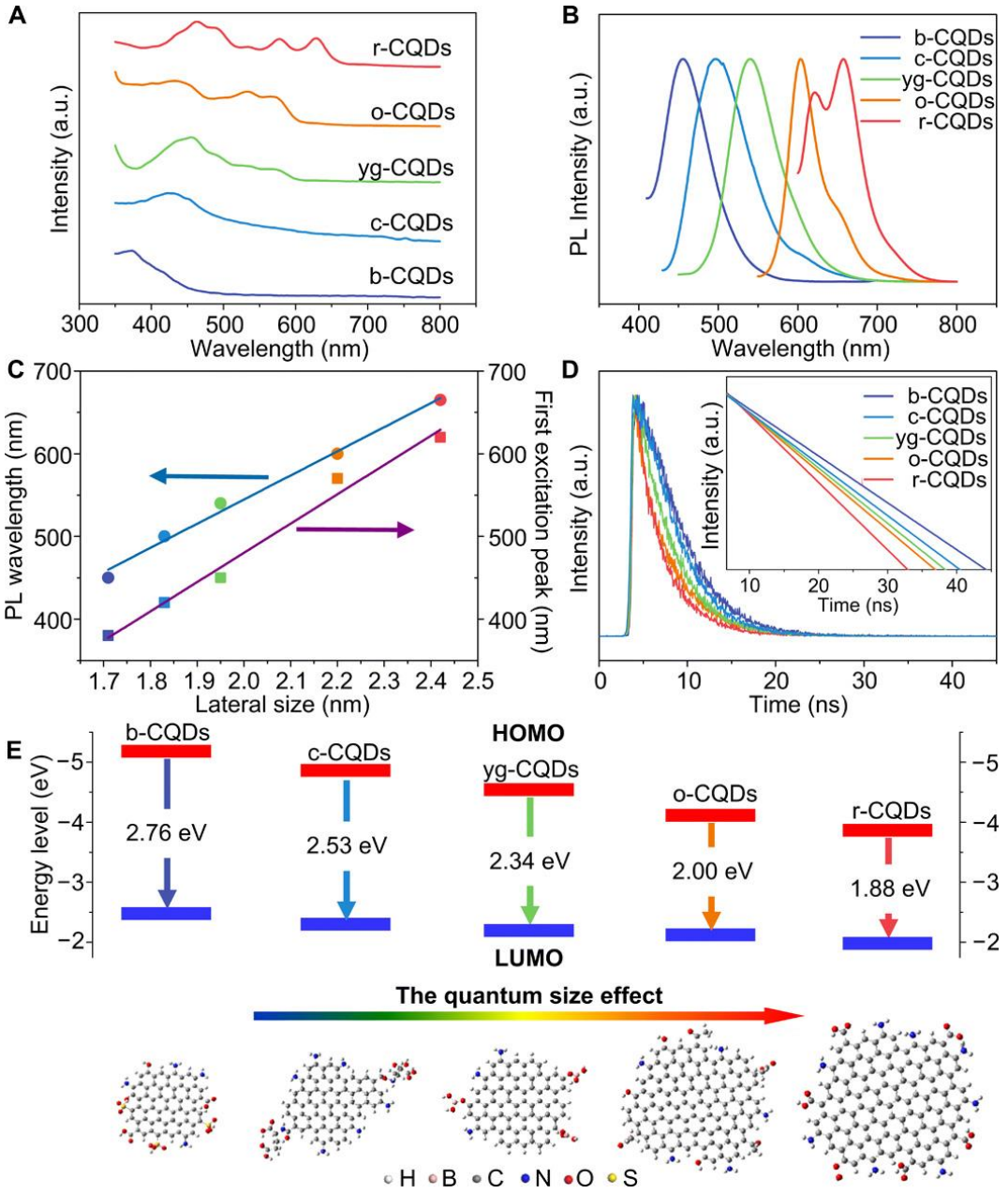


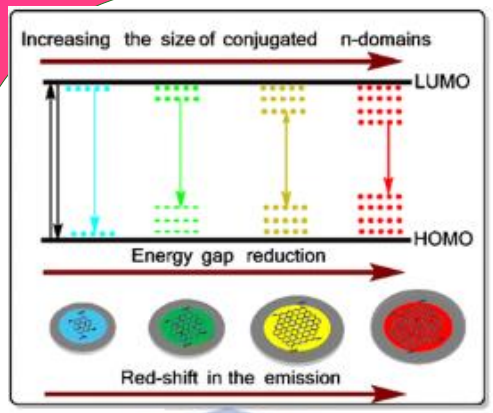
o-phenylenediamine (oPD)
+
Ethanol

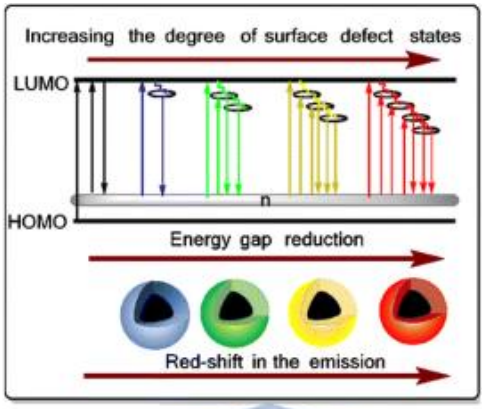
4-aminobenzenesulfonic acid (4-ABSA),
folic acid (FA),
boric acid (BA),
acetic acid (AA),
terephthalic acid (TPA),
tartaric acid (TA)

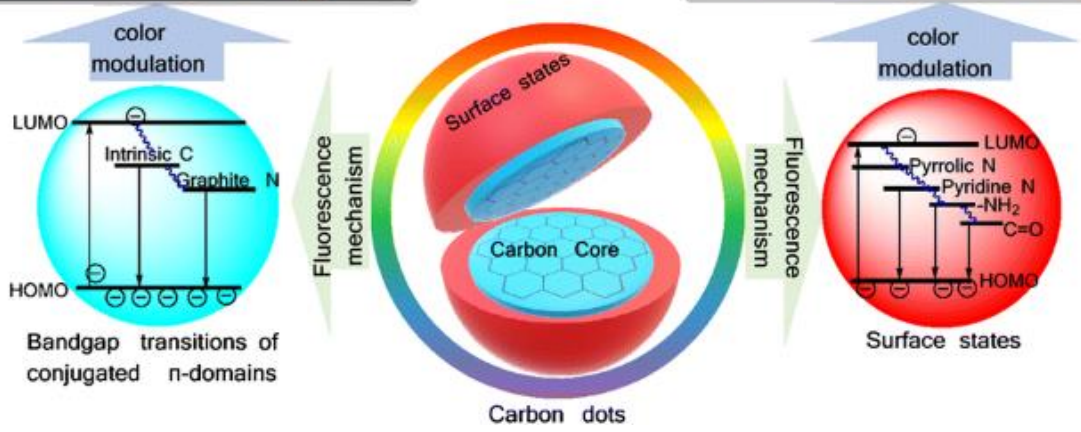
SCIENCE ADVANCES, 2 Oct 2020, Vol 6, Issue 40, DOI: 10.1126/sciadv.abb677


A
1 2 3
Lateral size (nm)
20 nm
B
1 2 3
Lateral size (nm)
20 nm
C
1 2 3
Lateral size (nm)
20 nm
D
1 2 3 4
Lateral size (nm)
20 nm
E
1 2 3 4
Lateral size (nm)
20 nm
F
0.21 nm
1 nm
G
0.21 nm
1 nm
H
0.21 nm
1 nm
I
0.21 nm
1 nm
J
0.21 nm
1 nm
K
0.2 0.6 1.0
Height (nm)
0.66 nm
0.00
500 nm
L
0.4 0.8 1.2
Height (nm)
0.67 nm
0.00
500 nm
M
0.0 0.4 0.8 1.2
Height (nm)
0.99 nm
0.00
500 nm
N
0.0 0.4 0.8 1.2
Height (nm)
0.77 nm
0.00
500 nm
O
0.0 0.5 1.0
Height (nm)
0.74 nm
0.00
500 nm


A
r-CQDs
o-CQDs
yg-CQDs
c-CQDs
b-CQDs
Intensity (a.u.)
300 400 500 600 700 800
Wavelength (nm)
B
b-CQDs
c-CQDs
yg-CQDs
o-CQDs
r-CQDs
PL Intensity (a.u.)
400 500 600 700 800
Wavelength (nm)
C
PL wavelength (nm)
First excitation peak (nm)
700 600 500 400
1.7 1.8 1.9 2.0 2.1 2.2 2.3 2.4 2.5
Lateral size (nm)
D
Intensity (a.u.)
b-CQDs
c-CQDs
yg-CQDs
o-CQDs
r-CQDs
10 20 30 40
Time (ns)
0 10 20 30 40
Time (ns)
E
Energy level (eV)
−5 −4 −3 −2
b-CQDs
2.76 eV
c-CQDs
2.53 eV
HOMO
yg-CQDs
2.34 eV
LUMO
o-CQDs
2.00 eV
r-CQDs
1.88 eV
The quantum size effect
H B C N O S

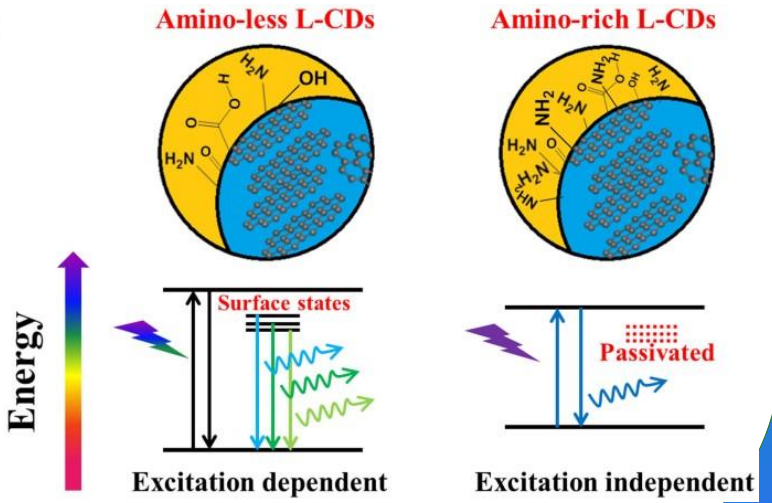


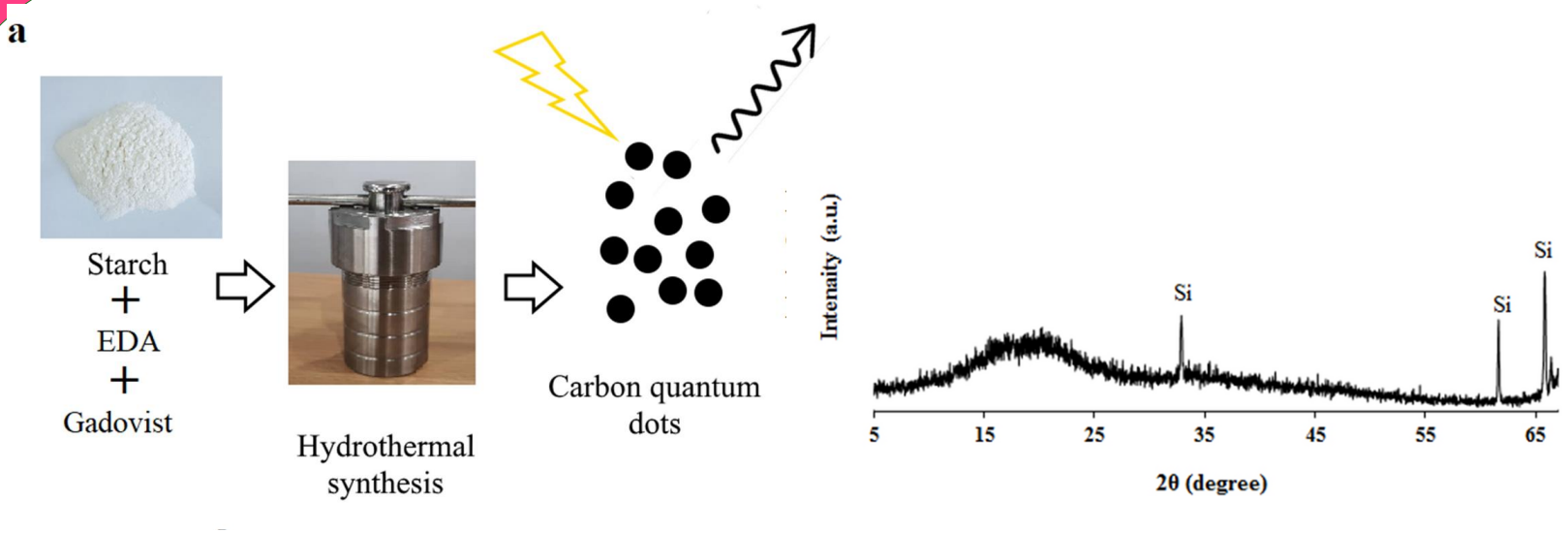


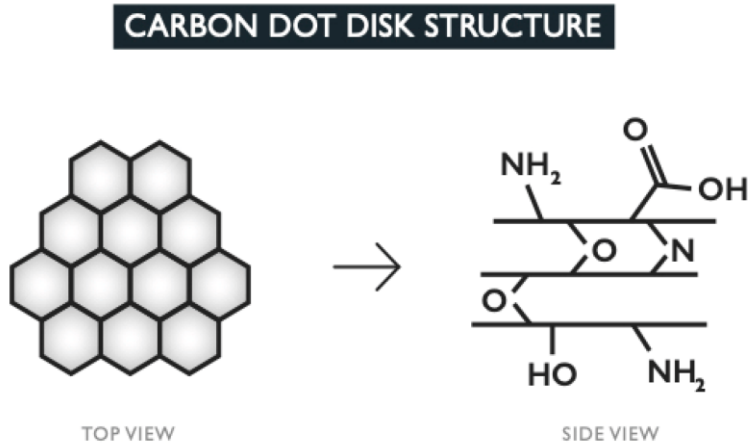


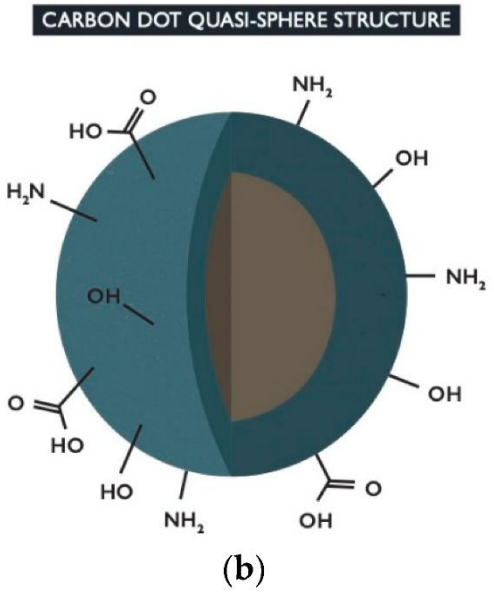
The bright surface defect-derived fluorescence of CDs is resulted from the recombination of electron–hole pairs in the strongly localized π and π* electronic levels of the sp^2 sites.

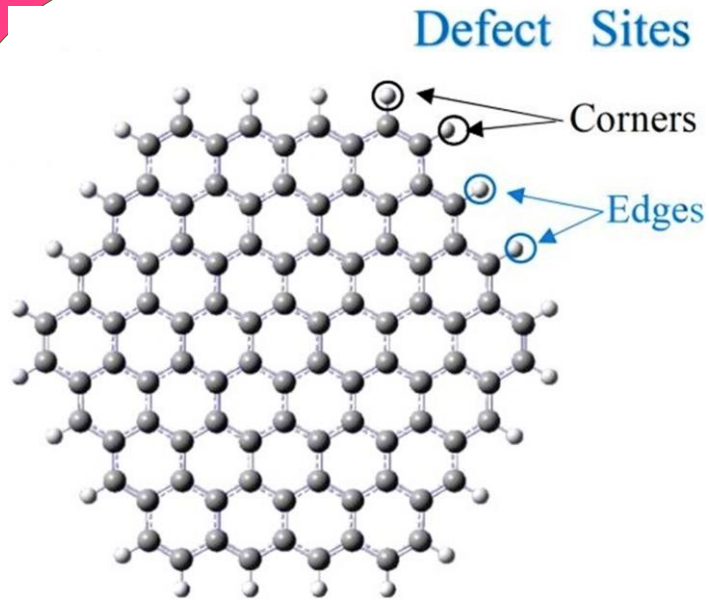
Surface defects of CDs are highly complicated, which are closely associated with both sp^2 and sp^3 hybridized carbons and other heteroatom-containing functional groups, such as dangling bonds, non-radiative states, and oxygen and nitrogen-related functional groups.

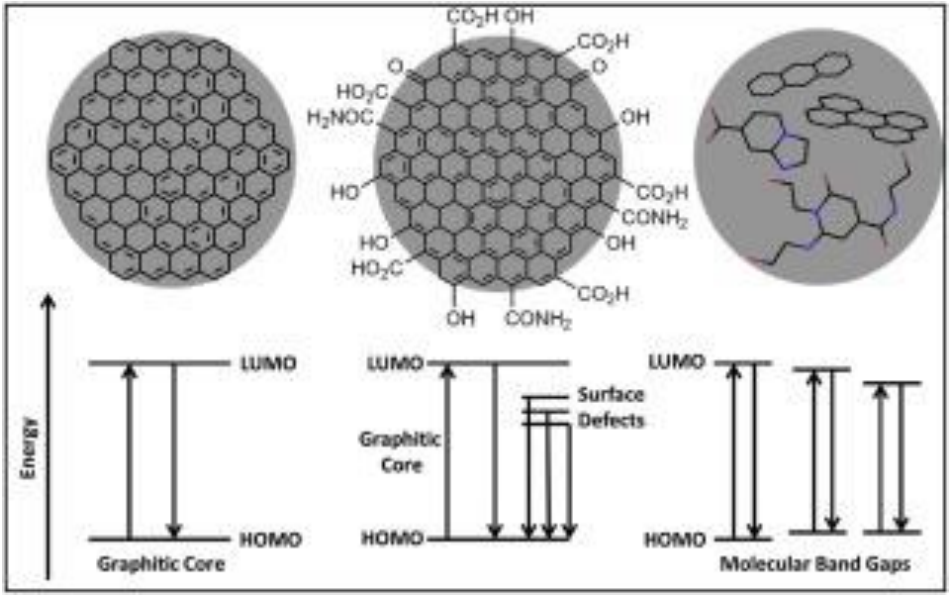


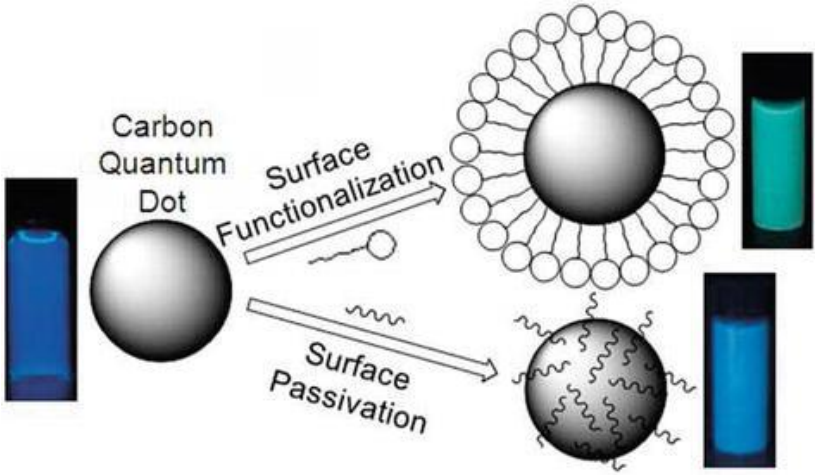

a
Starch
+
EDA
+
Gadovist
Hydrothermal synthesis
Carbon quantum dots
Intenaity (a.u.)
Si
Si
Si
5
15
25
35
45
55
65
2θ (degree)

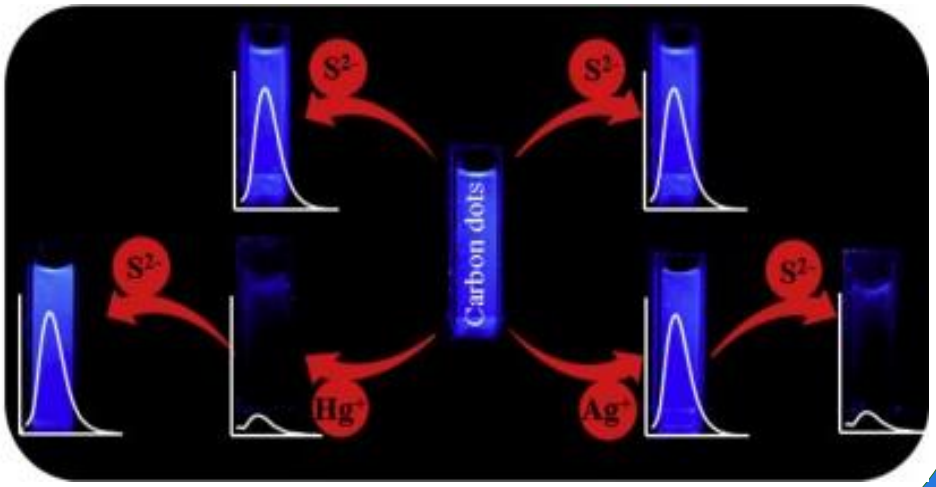

CARBON DOT DISK STRUCTURE
TOP VIEW
SIDE VIEW


CARBON DOT QUASI-SPHERE STRUCTURE
(b)


Defect Sites
Corners
Edges

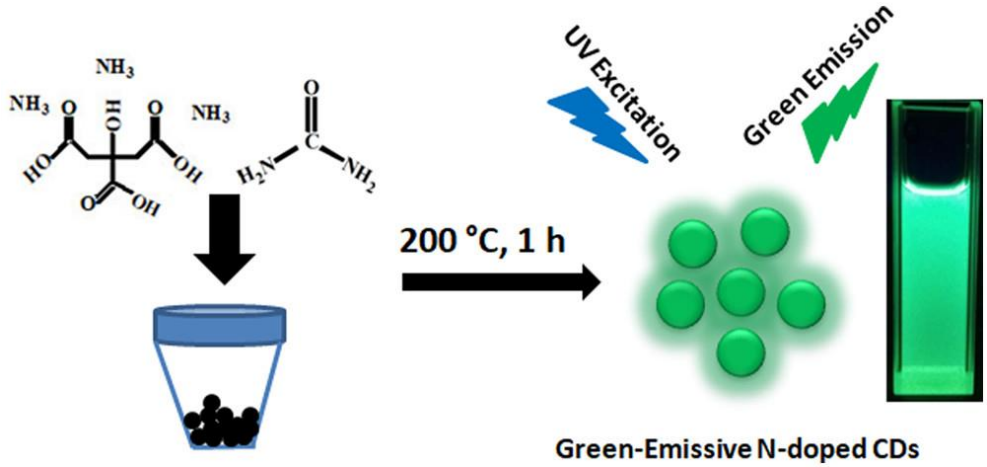

LUMO
HOMO
Energy
Graphitic Core
Surface Defects
Molecular Band Gaps

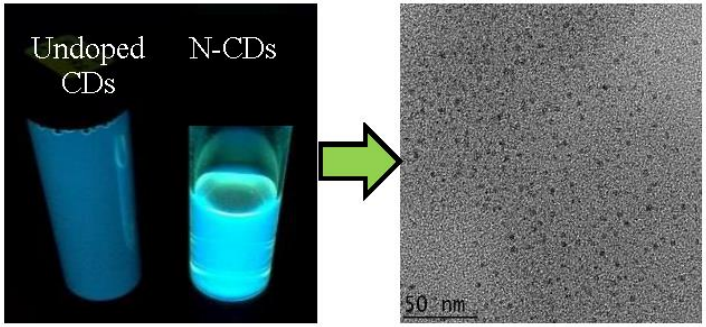

Carbon Quantum Dot
Surface Functionalization
Surface Passivation

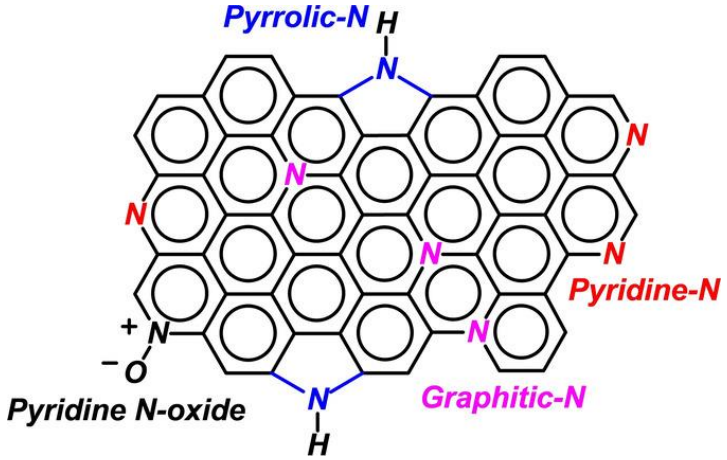

Carbon dots
S2-
Hg2+
Ag+

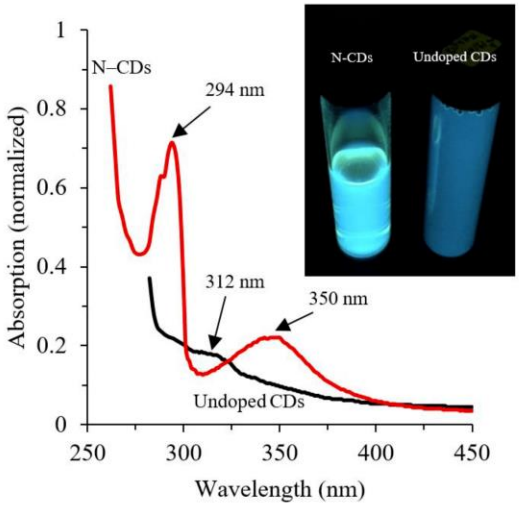
Ion sensing

Nitrogen doped CQDs

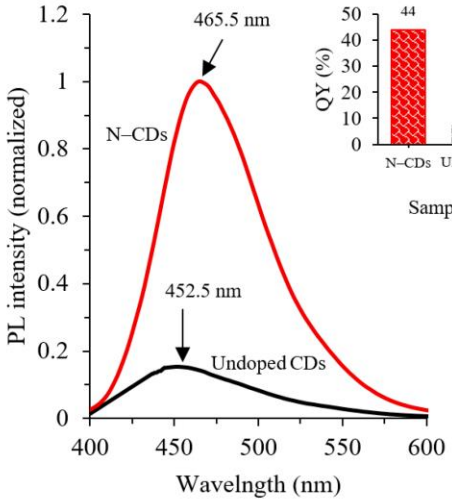








(a)



(b)

Microwave synthesis of CQDs

The molecules undergo excitation with electromagnetic radiation during Microwave synthesis.

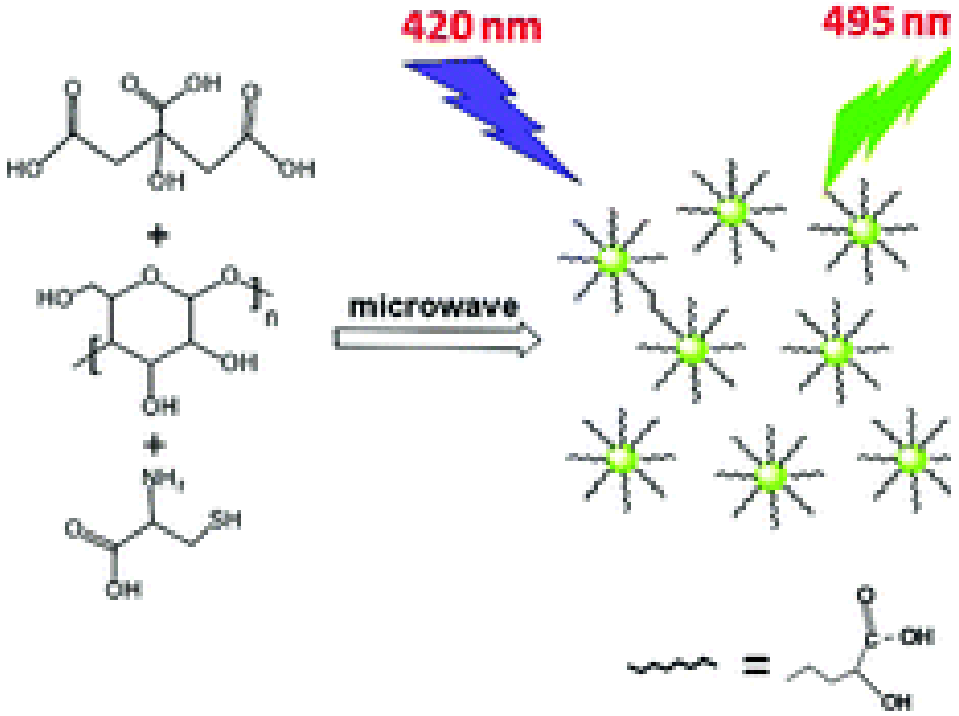
The water molecule is the target for microwave ovens in the home; like any other molecule with a dipole, it absorbs microwave radiation.

Microwave radiation is converted into heat with high efficiency, so that "superheating" (external link) becomes possible at ambient pressure.

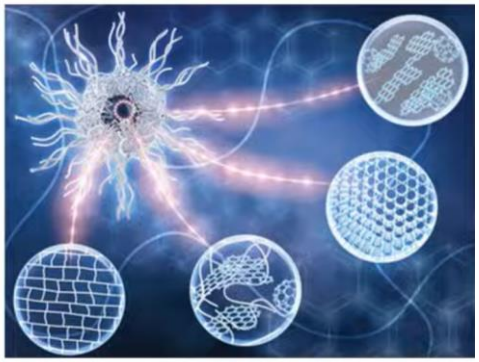
citric acid

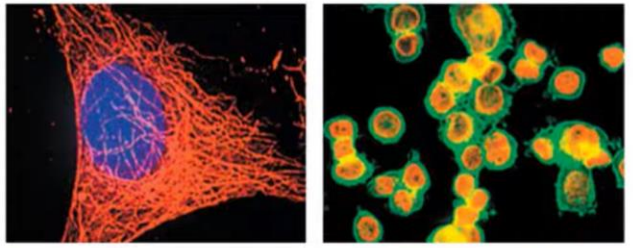
dextrin

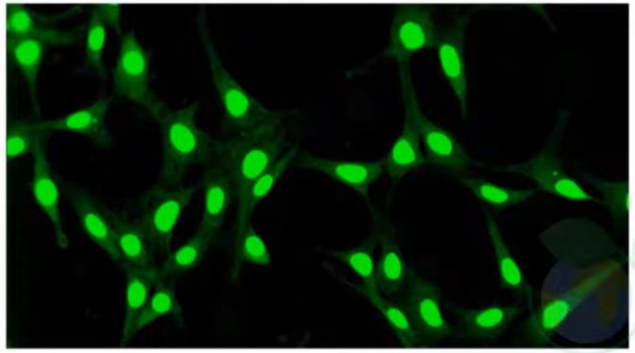
l-cysteine

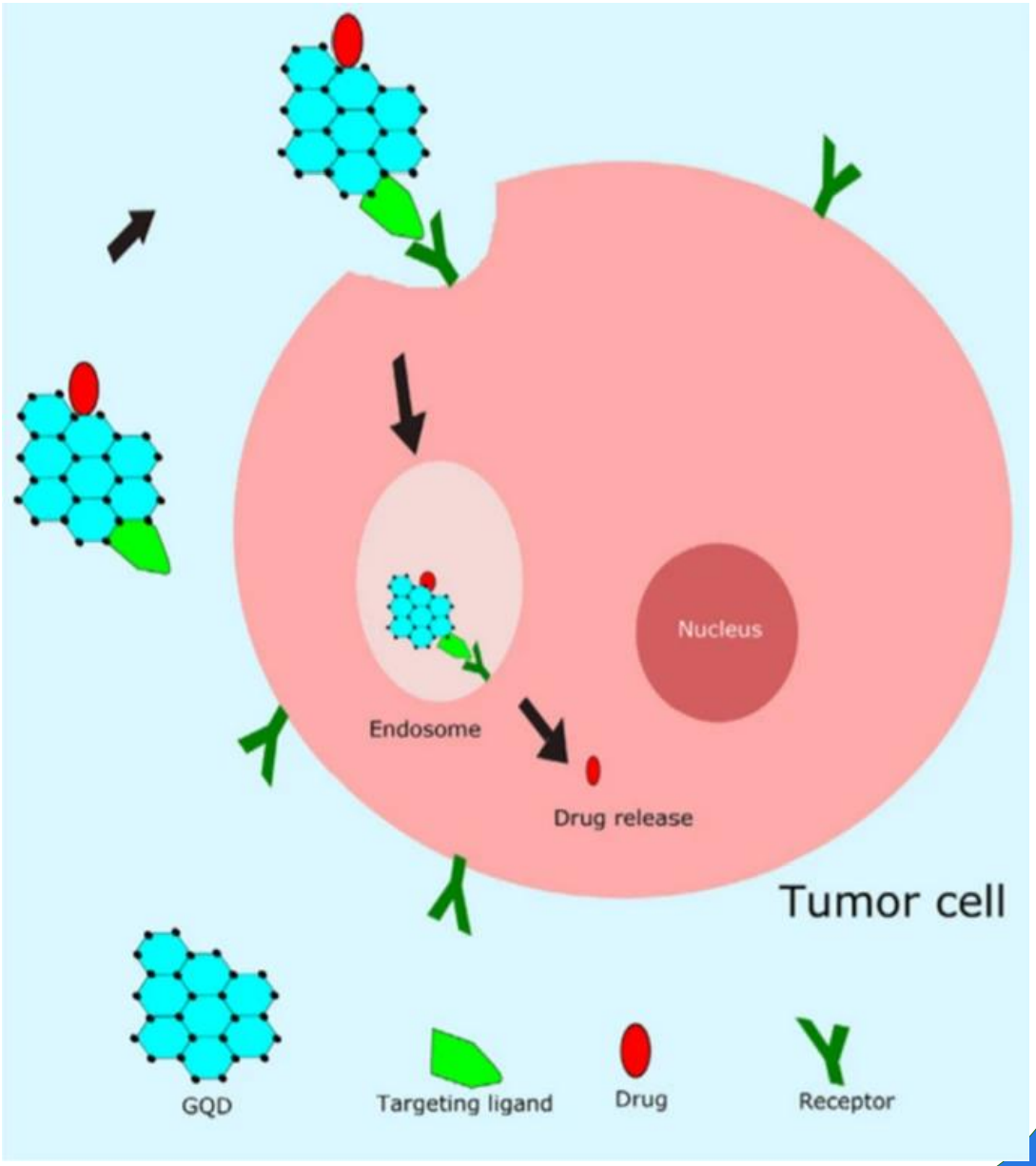


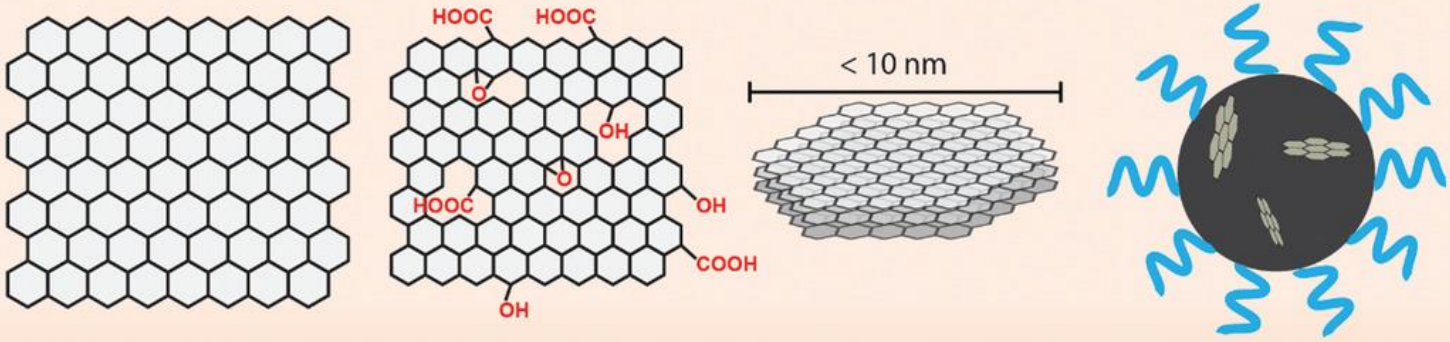
Cell Imaging Using Carbon Dots

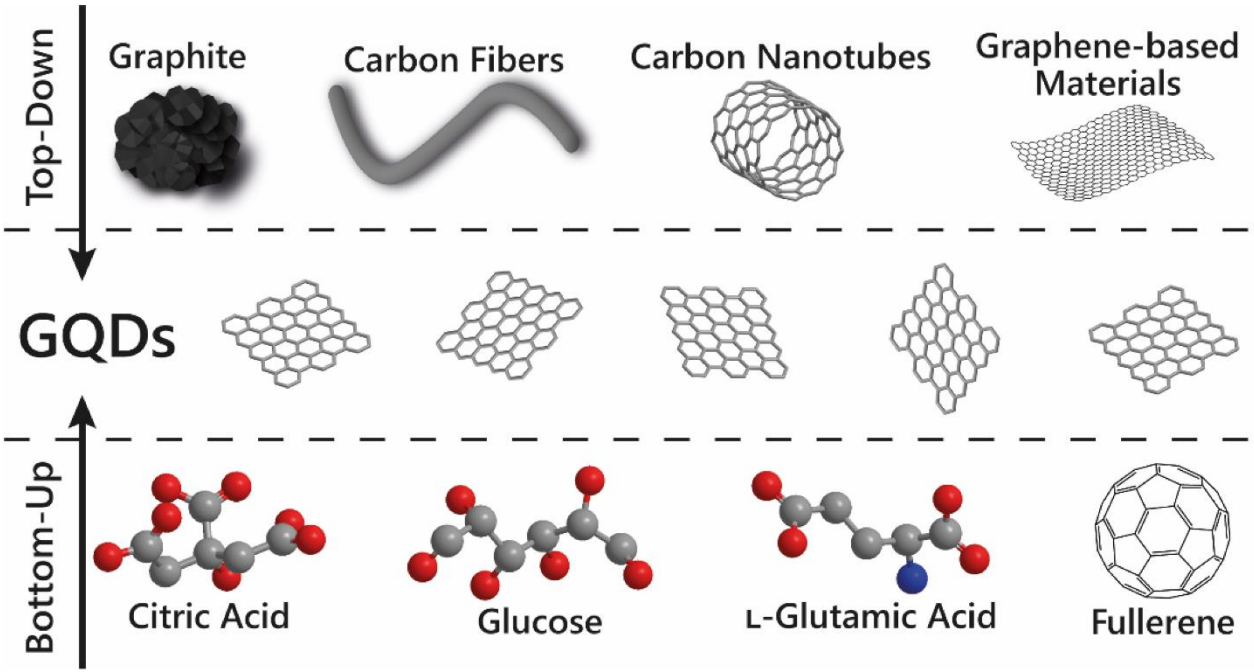




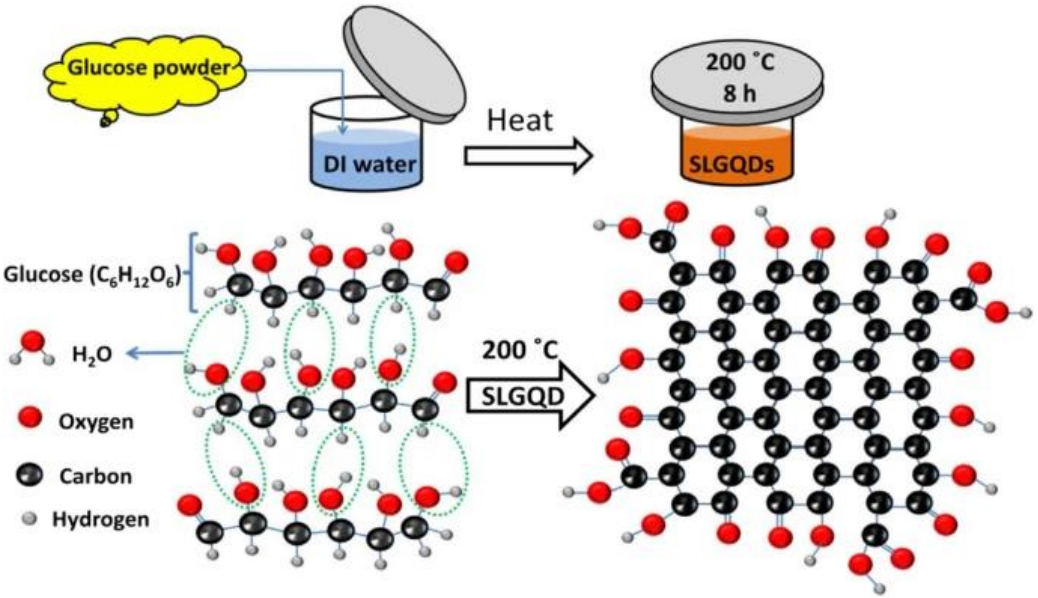


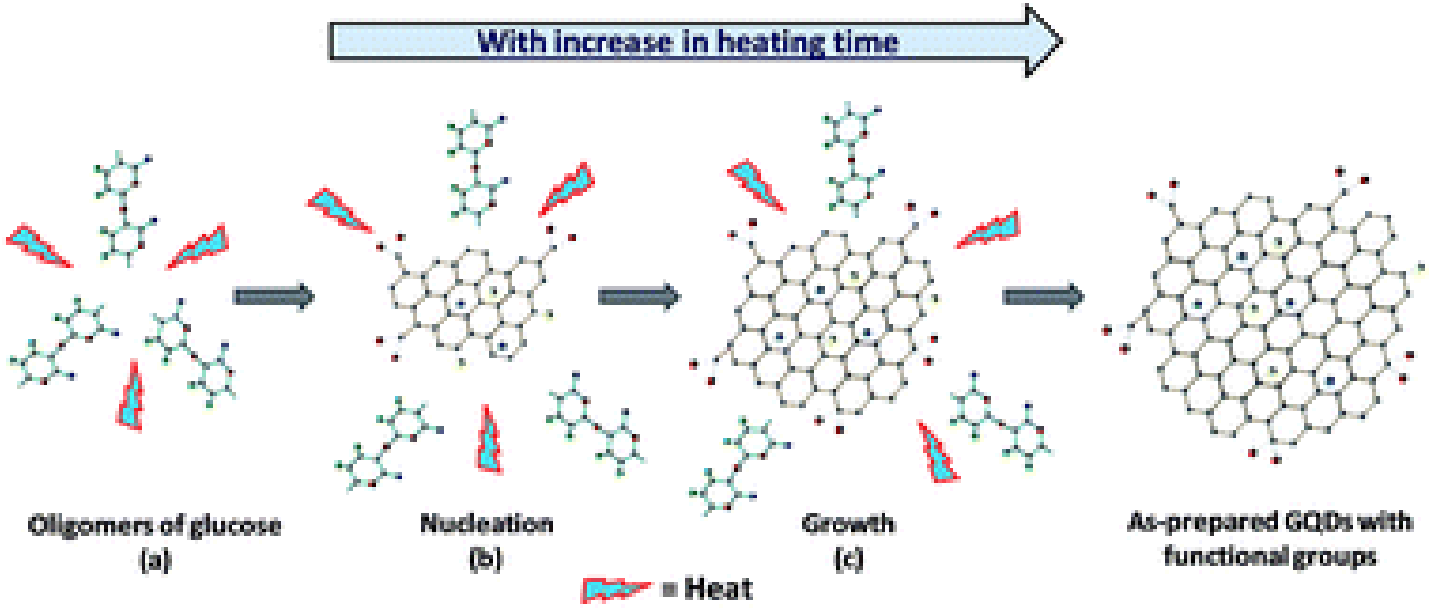



HOOC
HOOC
O
OH
O
HOOC
OH
COOH
OH
< 10 nm
Graphene
Graphene oxide
Graphene quantum dots
Carbon quantum dots

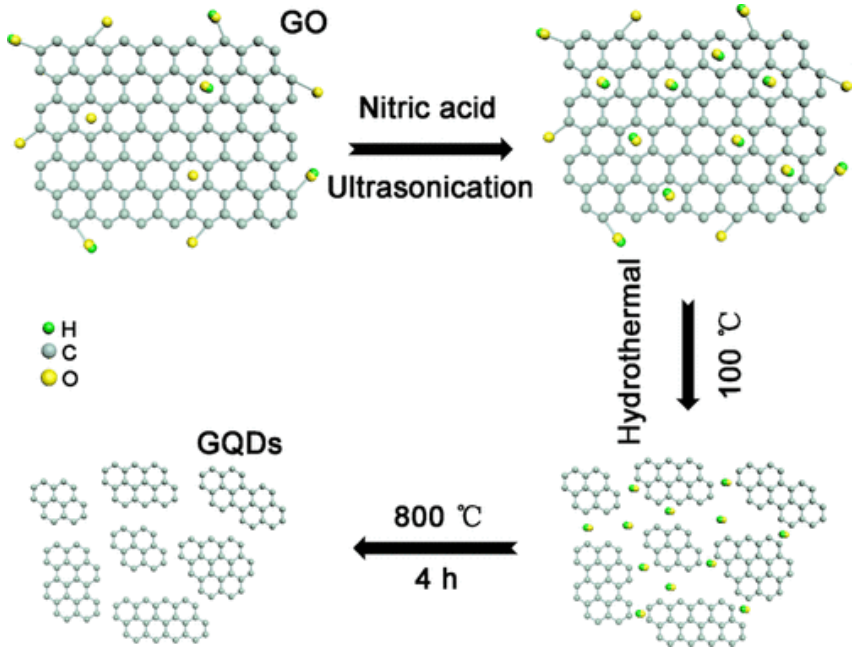

Top-Down
Graphite
Carbon Fibers
Carbon Nanotubes
Graphene-based Materials
GQDs
Bottom-Up
Citric Acid
Glucose
L-Glutamic Acid
Fullerene

Hydrothermal method

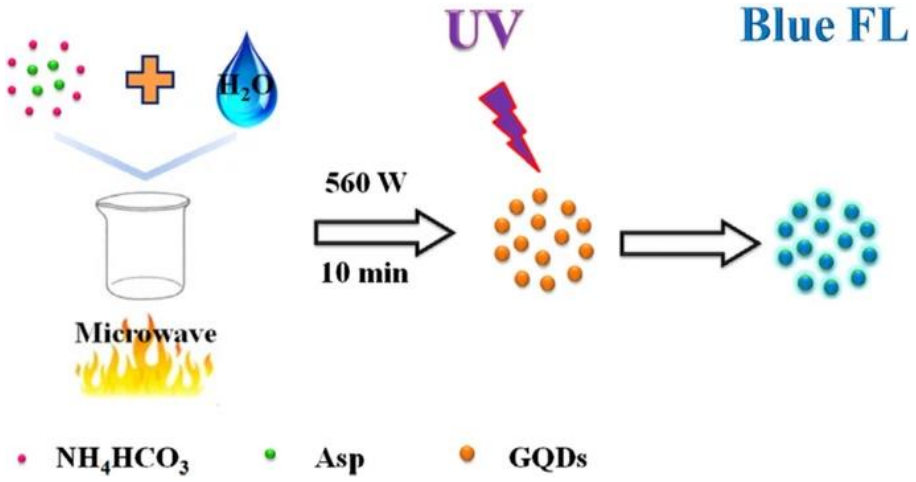


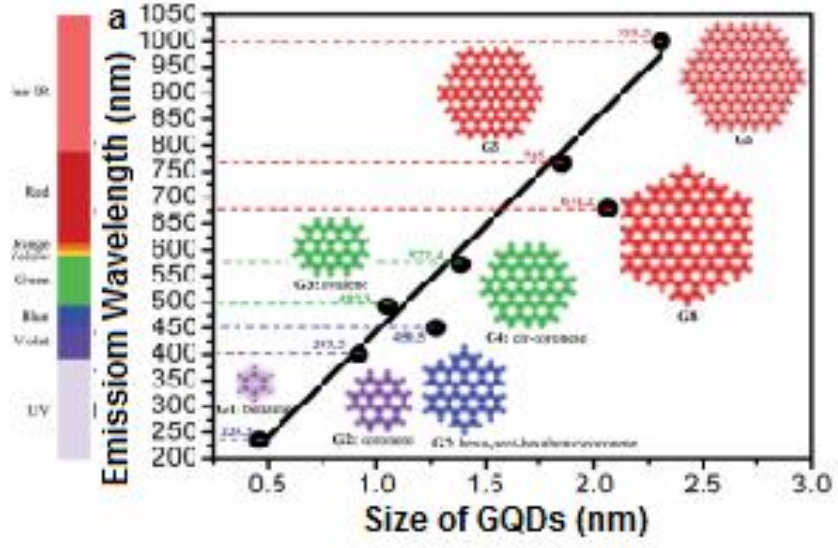


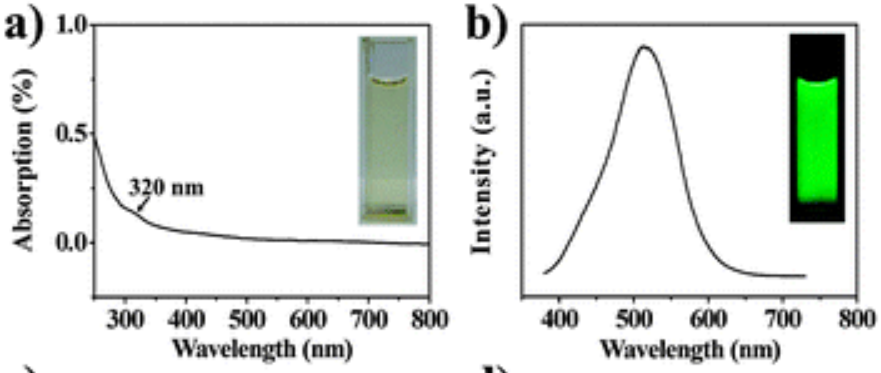
Hydrothermal method

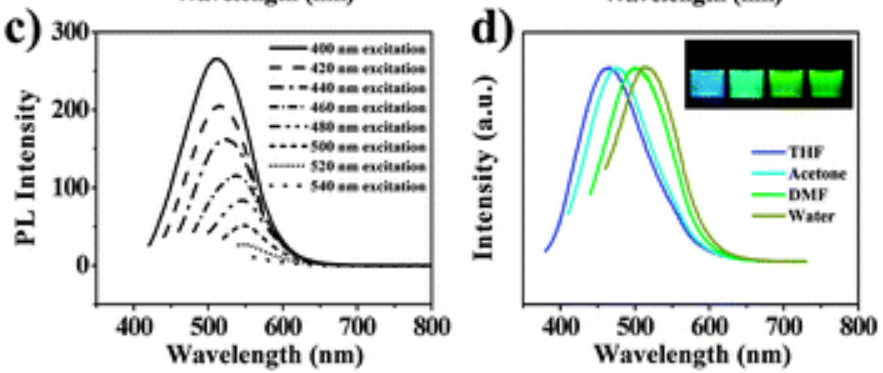


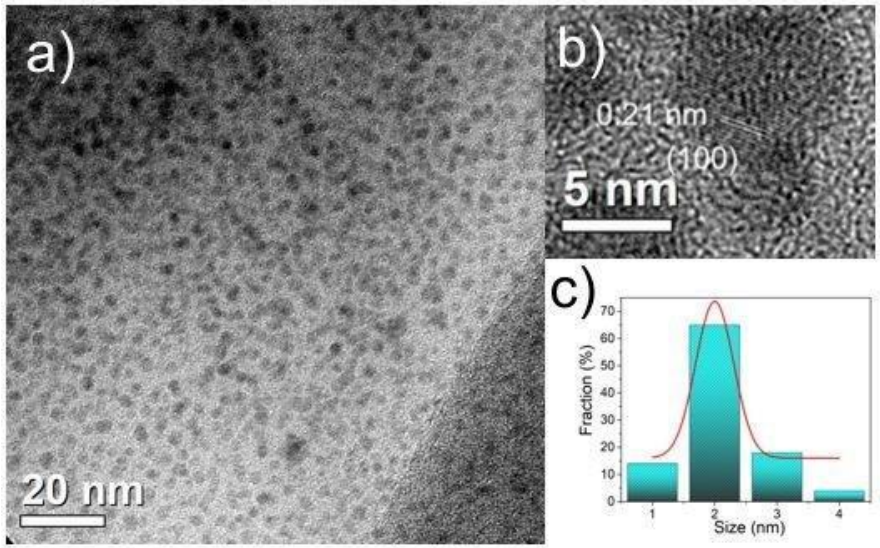
Microwave heating

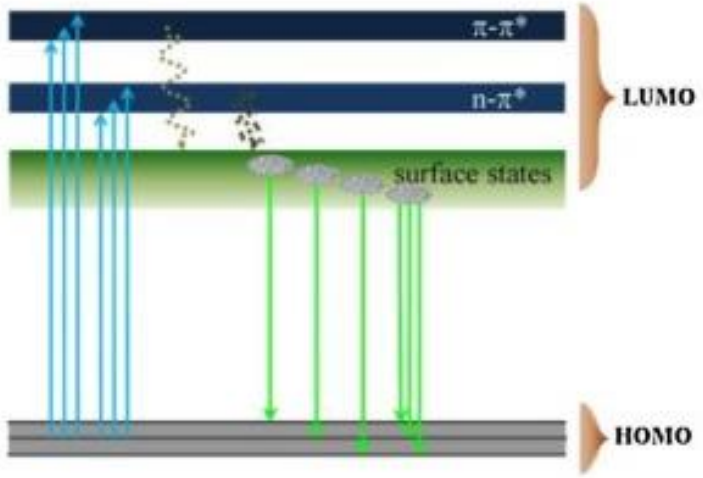


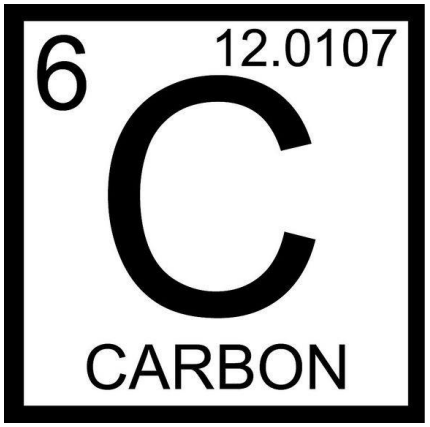

a
Emission Wavelength (nm)
Size of GQDs (nm)
Red
Green
Blue
Violet
UV

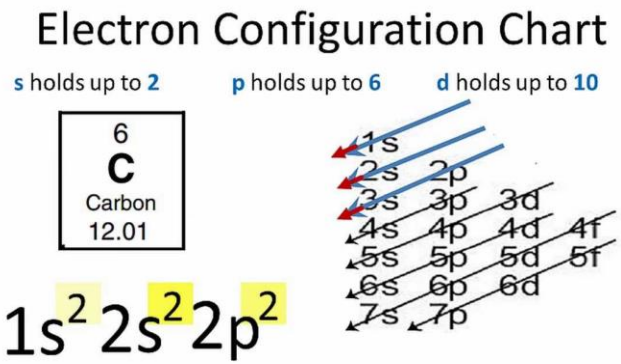

a)
Absorption (%)
320 nm
Wavelength (nm)
b)
Intensity (a.u.)
Wavelength (nm)

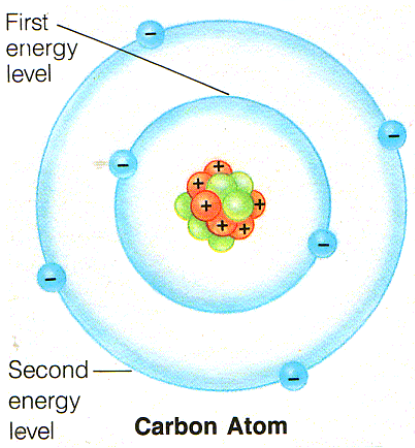

c)
PL Intensity
400 nm excitation
420 nm excitation
440 nm excitation
460 nm excitation
480 nm excitation
500 nm excitation
520 nm excitation
540 nm excitation
Wavelength (nm)
d)
Intensity (a.u.)
THF
Acetone
DMF
Water
Wavelength (nm)


a)
20 nm
b)
0.21 nm
(100)
5 nm
c)
Fraction (%)
Size (nm)


π-π*
n-π*
surface states
LUMO
HOMO



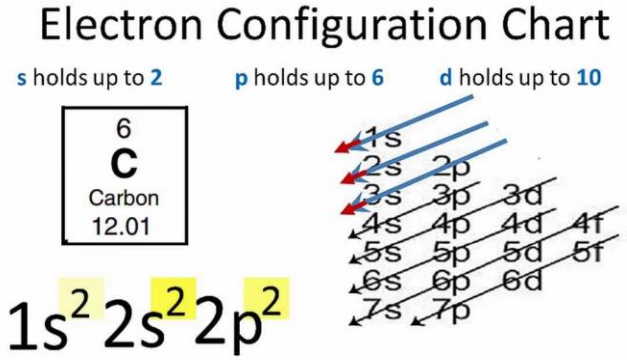


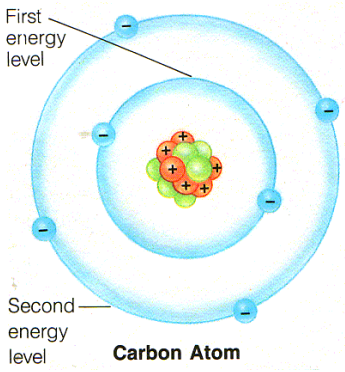


Carbon based Structures and Applications

Carbon based nanostructures

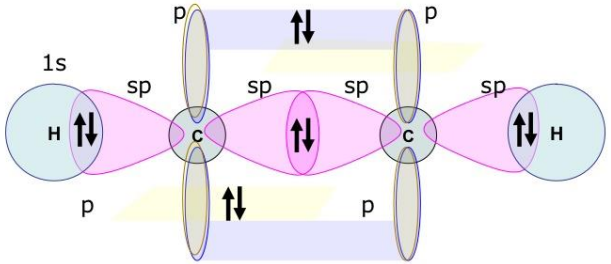
Carbon electronic structure:



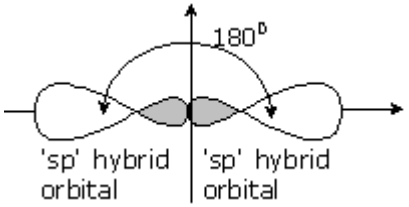


HYBRIDIZATION

Example: **Ethyne (C_2H_2)**



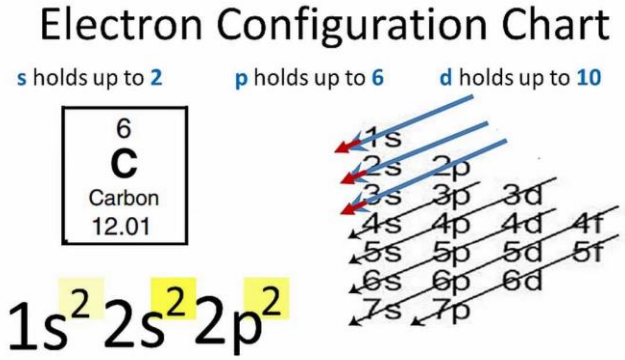
Carbon bonding:

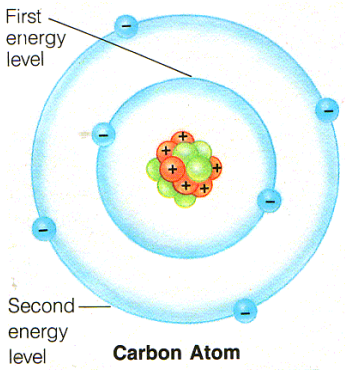


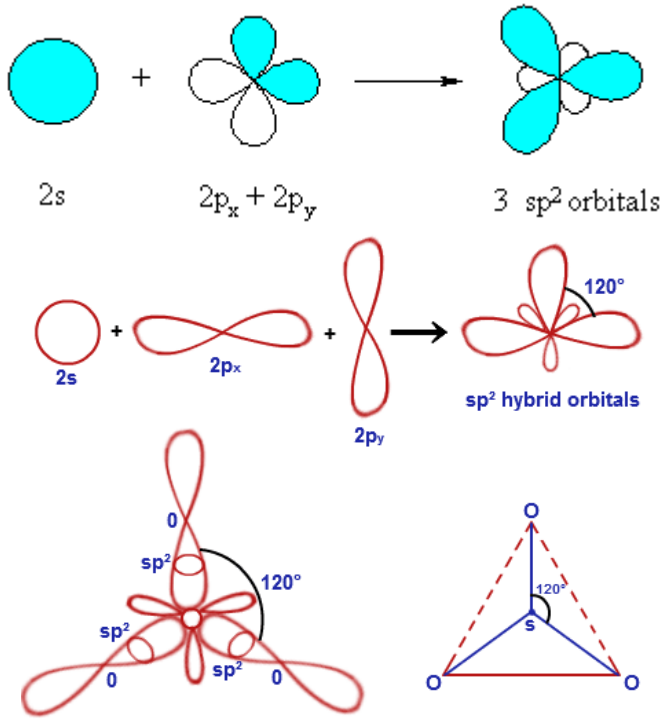
- Carbon has four valence electrons !
- Energetically preferred arrangements of these electrons are so-called *sp*-hybridized electron wavefunctions, which can then form covalent chemical bonds with other atoms.
- *sp* hybridization: 2 bonds, bond angle 180°, eg., acetylene C_2H_2.
- sp^2 hybridization: 3 bonds in plane, bond angle 120°, eg., ethylene C_2H_4.
- sp^3 hybridization: 4 bonds in 3D, bond angle $\cos^{-1}(-1/3) \approx 109.5°$, *e.g.*, methane CH_4.
- Carbon bonds are very strong (4 eV per bond) if they are bonded to other carbon atoms.

Carbon based nanostructures

Carbon electronic structure:





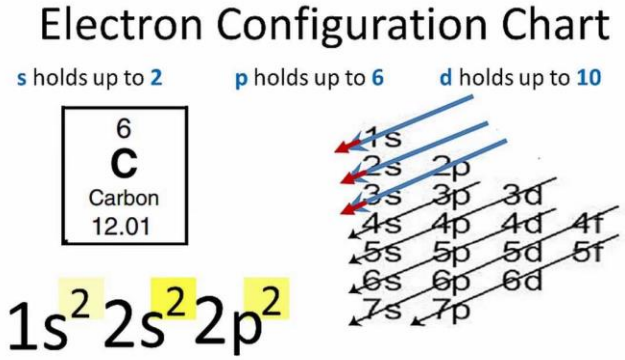


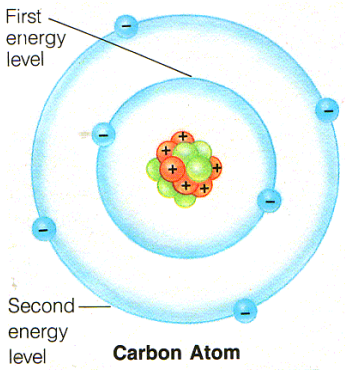
Carbon bonding:

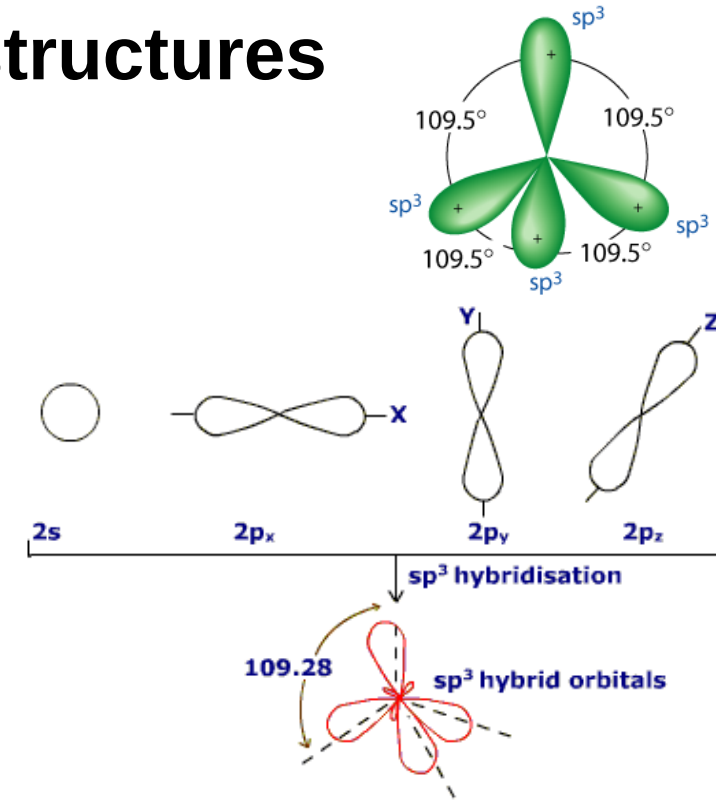
- Carbon has four valence electrons !
- Energetically preferred arrangements of these electrons are so-called *sp*-hybridized electron wavefunctions, which can then form covalent chemical bonds with other atoms.
- *sp* hybridization: 2 bonds, bond angle 180°, eg., acetylene C_2H_2.
- sp^2 hybridization: 3 bonds in plane, bond angle 120°, eg., ethylene C_2H_4.
- sp^3 hybridization: 4 bonds in 3D, bond angle $\cos^{-1}(-1/3) \approx 109.5°$, *e.g.*, methane CH_4.
- Carbon bonds are very strong (4 eV per bond) if they are bonded to other carbon atoms.

Carbon based nanostructures

Carbon electronic structure:







Carbon bonding:

- Carbon has four valence electrons !
- Energetically preferred arrangements of these electrons are so-called *sp*-hybridized electron wavefunctions, which can then form covalent chemical bonds with other atoms.
- *sp* hybridization: 2 bonds, bond angle 180°, eg., acetylene C_2H_2.
- sp^2 hybridization: 3 bonds in plane, bond angle 120°, eg., ethylene C_2H_4.
- sp^3 hybridization: 4 bonds in 3D, bond angle $\cos^{-1}(-1/3) \approx 109.5°$, *e.g.*, methane CH_4.
- Carbon bonds are very strong (4 eV per bond) if they are bonded to other carbon atoms.

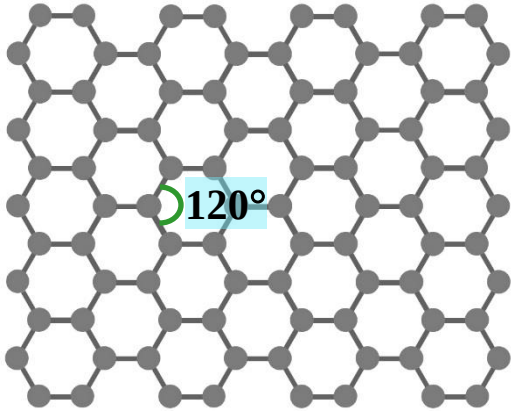
Bulk Carbon Structures

What happens when we form a solid out of these bonding types?

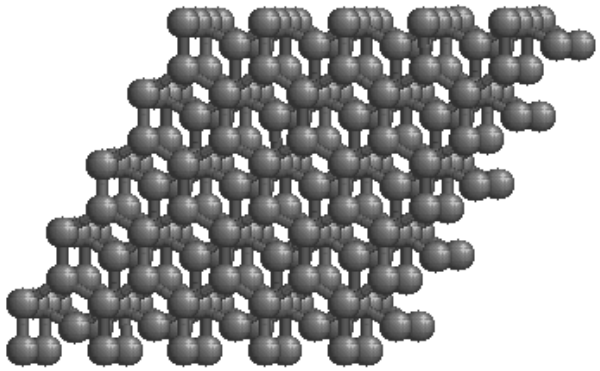
→ ***sp*:** linear chain of C (possible, but cannot easily form a solid)

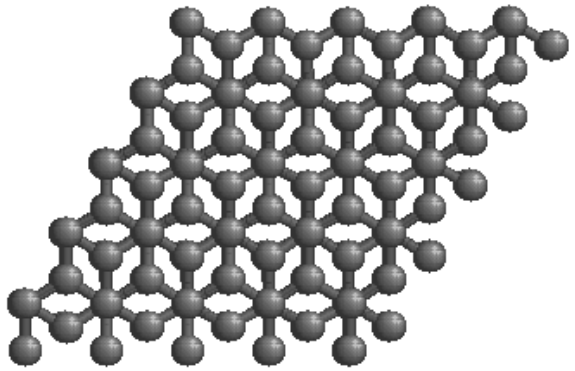
→ ***sp*²:** bonds are in the same plane, can form 2-d C-plane. With an angle of 120° between bonds, a honeycomb (open hexagon) network can be formed. "graphene" sheet (stacks of graphene sheets → graphite (ground state of C) – semimetal.

→ ***sp*³**: tetrahedral sp^3 arrangement leads to 3-d solid (diamond).



Graphene





Graphite

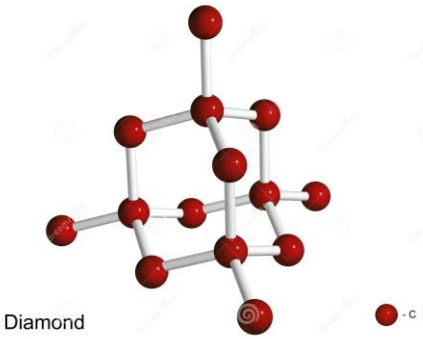
Bulk Carbon Structures

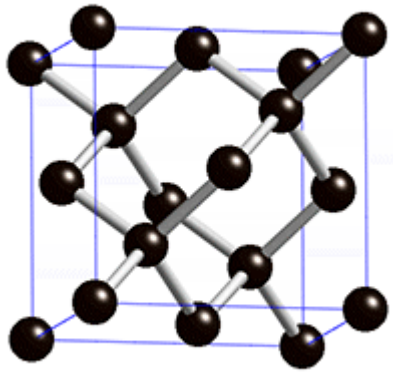
What happens when we form a solid out of these bonding types?

→ ***sp*:** linear chain of C (possible, but cannot easily form a solid)

→ ***sp*²:** bonds are in the same plane, can form 2-d C-plane. With an angle of 120° between bonds, a honeycomb (open hexagon) network can be formed. "graphene" sheet (stacks of graphene sheets → graphite (ground state of C) – semimetal.

→ ***sp*³**: tetrahedral sp^3 arrangement leads to 3-d solid (diamond).





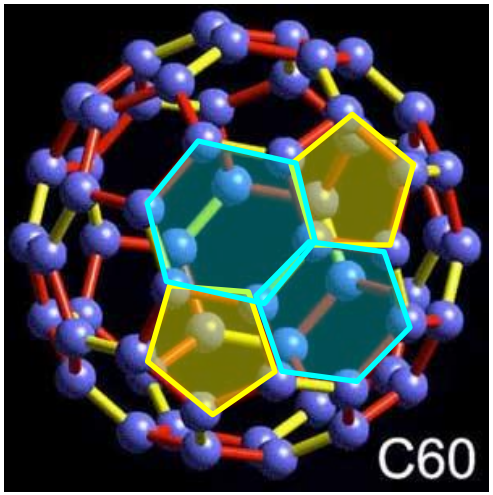
Diamond

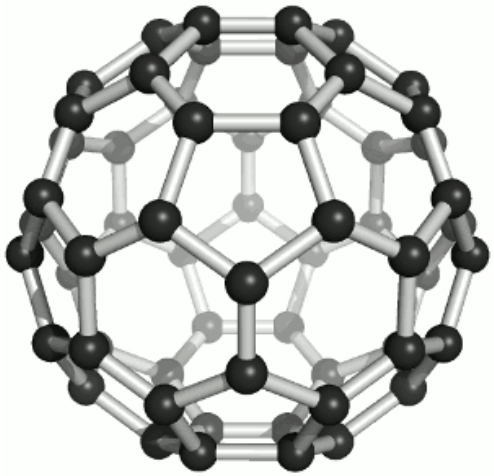
59.6 carat diamond "Pink Star"
US$71.2 Million = Rs. 464 Crores
On April 04, 2017

Fullerenes

Carbon based nanostructures

The discovery of the C_{60} fullerene molecule in 1985 (Nobel prize in 1996; Kroto, Curl and Smalley) opened up the field of fullerene research.



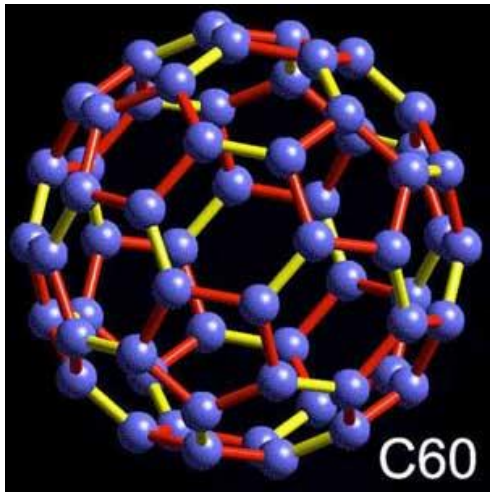


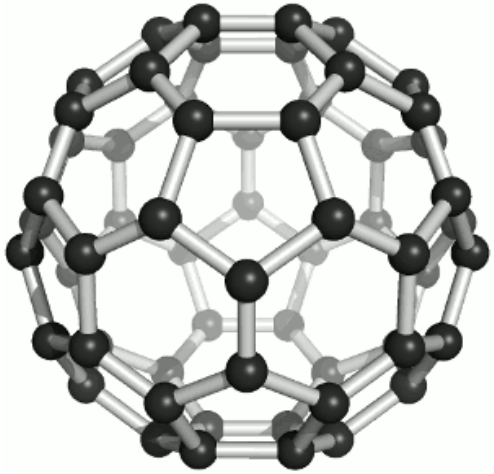
- Sixty carbon atoms
- Five-membered rings (12) are isolated by six-membered rings (20)
- Van der Waals diameter is about 1.1 nm

- Appears like soccer ball (called as buckyball)
- Filled with six member (two comes close) and five member (only one comes close) carbon rings ➔ Called as Fullerenes
- Exceptionally stable & strong due to its high symmetry (& the C bonds being pretty close to the ideal sp^2 covalent bonding). So it is a semiconductor
- Name was an homage to Buckminster Fuller, whose geodesic domes it resembles

Carbon based nanostructures

The discovery of the C_{60} fullerene molecule in 1985 (Nobel prize in 1996) opened up the field of fullerene research.



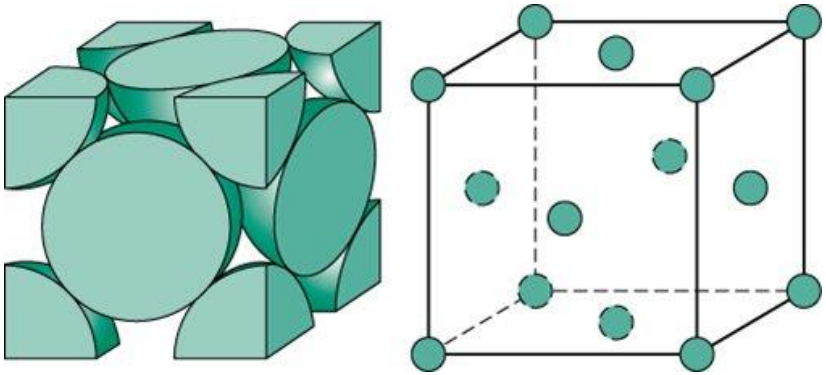


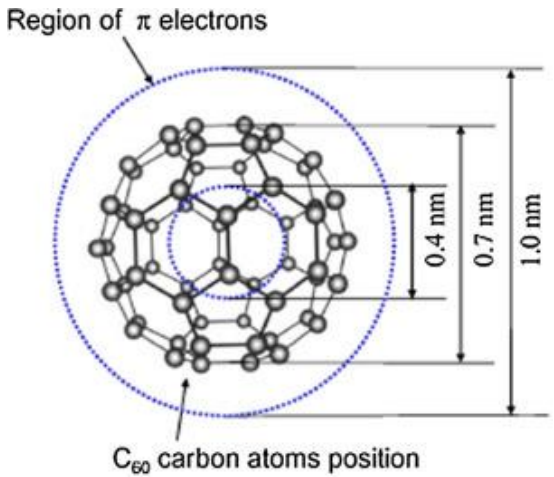
- **Sixty carbon atoms**
- **Five-membered rings isolated by six-membered rings**
- **van der Waals diameter is about 1.1 nm**
- **Nucleus to nucleus diameter of a C_{60} molecule is about 0.71 nm**

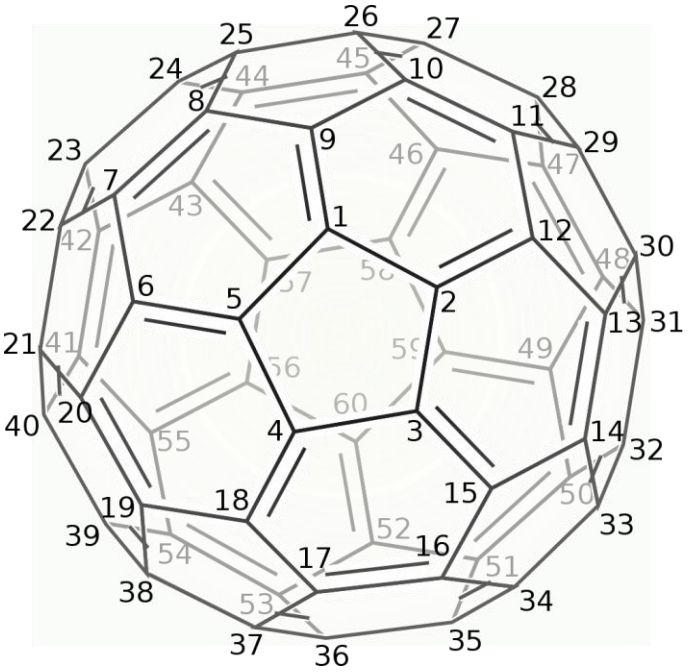
- **Appears like soccer ball (called as buckyball)**
- **Filled with six member (two comes close) and five member (only one comes close) carbon rings ➔ Called as Fullerenes**
- **Exceptionally stable & strong due to its high symmetry (& the C bonds being pretty close to the ideal sp^2 covalent bonding). So it is a semiconductor**
- **Name was an homage to Buckminster Fuller, whose geodesic domes it resembles**

Carbon based nanostructures

- A three dimensional network of carbon atoms
- Containing pentagonal and hexagonal rings in which no two pentagons share an edge
- Each atom connected to exactly three neighbors with an angle of 120°







Carbon based nanostructures

1. Buckyball cluster:

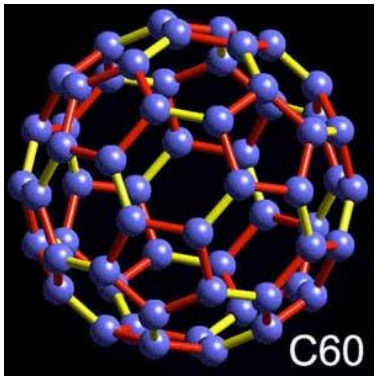
2. **Nanotubes**: Hollow tubes of very small dimensions (having single or multiple walls)

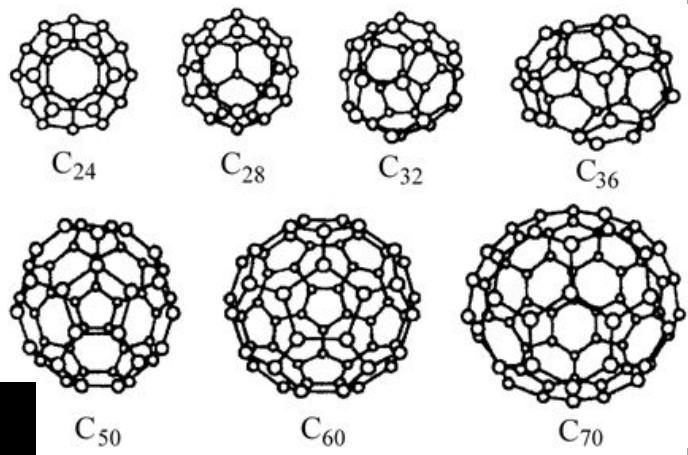
3. **Megatubes:** Larger in diameter and prepared with walls of different thicknesses

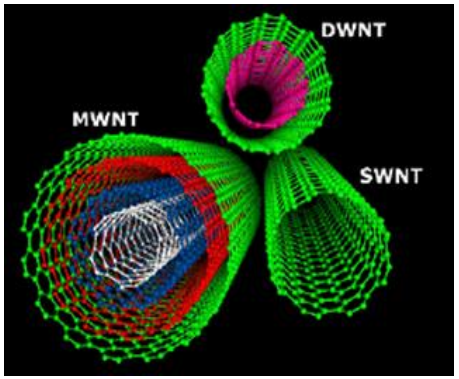
4. Fullerene rings

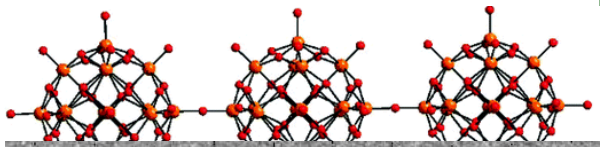
5. **Linked "ball-and-chain" dimers**: Two buckyballs linked by a carbon chain

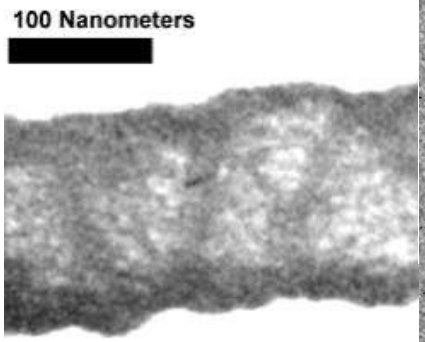
6. **Nano "onions"**: Spherical particles based on multiple carbon layers surrounding a buckyball core

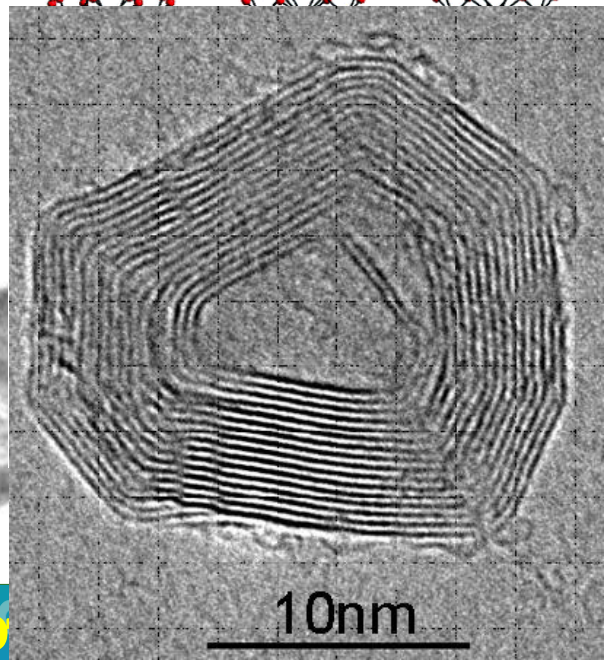








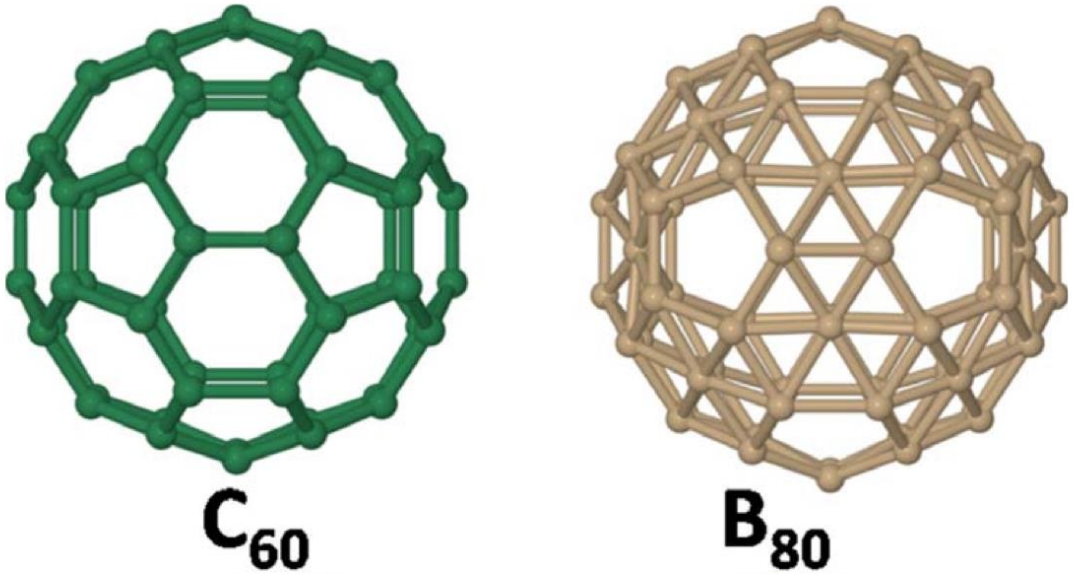




Boron BuckyBall

Similar to Carbon, Boron also forms a type of buckyball (found in 2007).

B_{80} structure with each atom forming 5 or 6 bonds is predicted to be more stable than C_{60} buckyball.

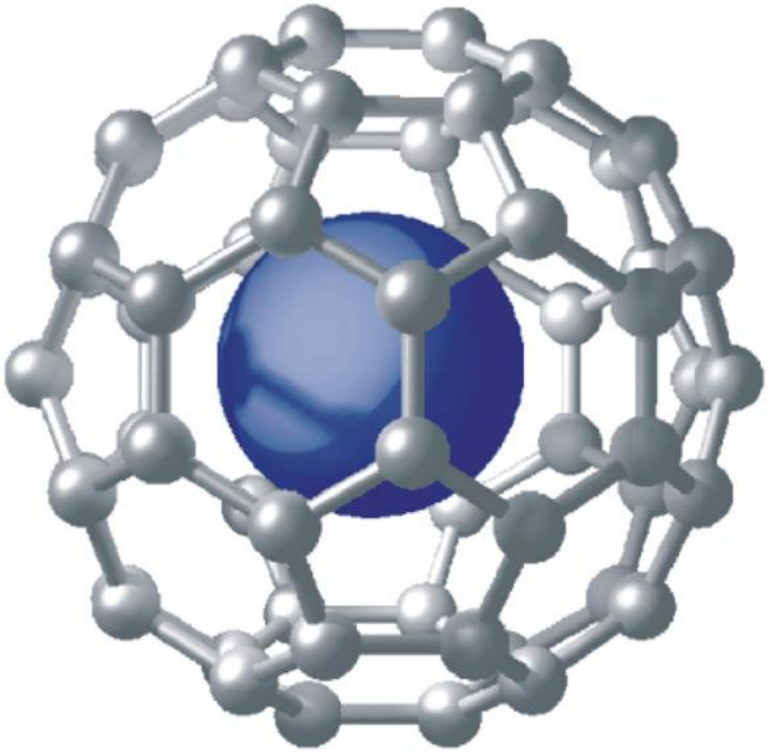


Szwacki et al, Phys. Rev. Lett. 98 (2007) 166804.

What is the use of buckyballs?

Fullerenes with material inside are called Cage compounds (or) Endohedral compounds

An atom of nitrogen?	d = ~ 120 pm Yes, definitely
A molecule of hydrogen?	d = ~ 150 pm Yes, definitely
A molecule of sulfuric acid?	d = ~ 700 pm Unlikely



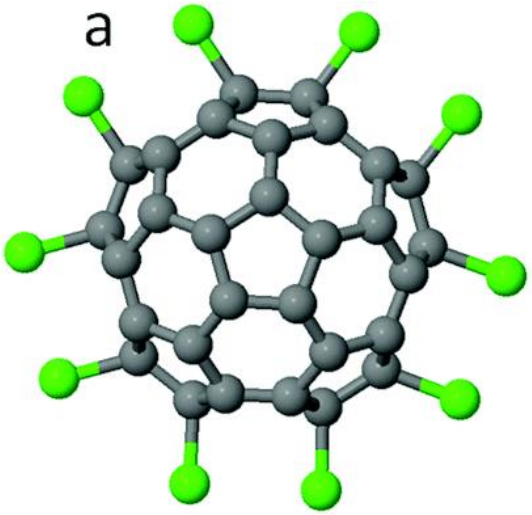
$M@C_{60}$, where M represents the atom inside of the cage

For example,

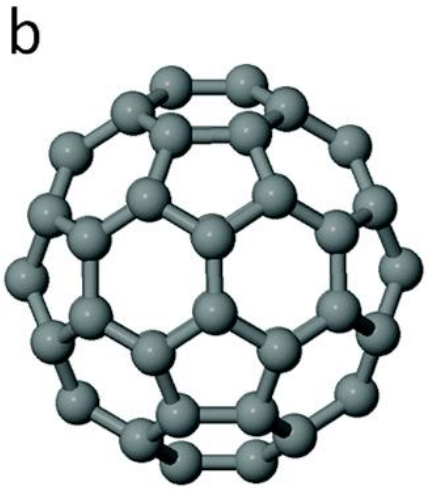
$N@C_{60}$; $La@C_{82}$

What is the use of buckyballs?

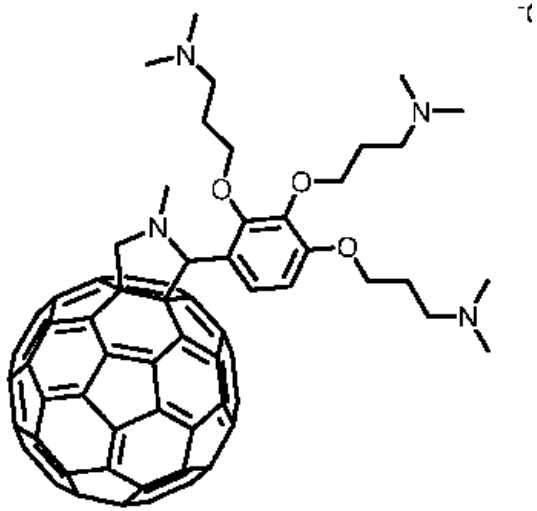
The materials placed exterior of the cage is called as Exohedral compounds



$C_{50}Cl_{10}$



C_{60}



C_{60}-N

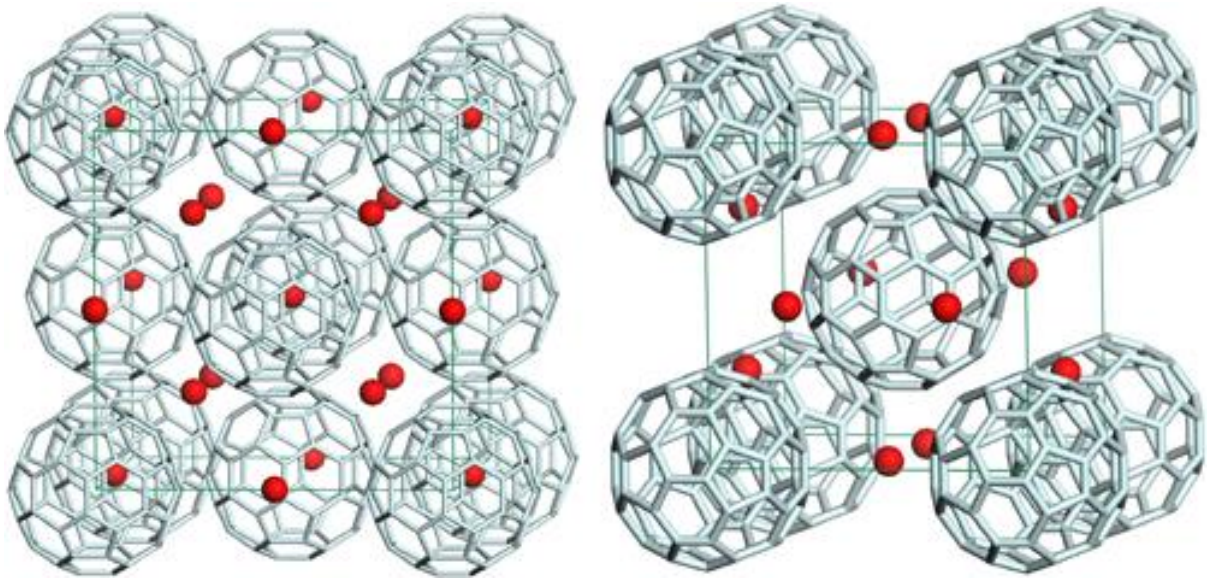
These materials offer the most potential and useful applications of fullerene materials

Interesting Properties/Applications of Fullerene

- **Bounce back to their original shape even after being subjected to 3000 atmosphere pressure.**

Interesting Properties/Applications of Fullerene

- **Bounce back to their original shape even after being subjected to 3000 atmosphere pressure.**



Spring 8 (2009 news): Grey spheres indicate fullerene. Red spheres indicate cesium atoms. e's cannot move freely between C_{60}, as adjacent C_{60} are relatively far apart (called a Mott insulator). The intermolecular distance of Cs_3C_{60} is shortened when pressure is applied, which allows electrons to jump to adjacent molecules. A strong attractive force simultaneously acts between the electrons, producing Cooper pairs and causing the transition to a superconductive state (T_c= 38 K).

Interesting Properties/Applications of Fullerene

- Experimental bulk modulus is 1 TPa (for diamond it is 442 GPa)
- Do not bond each other through chemical bonding. This makes them to use as good lubricants.

- Good materials as catalyst: Conversion of Ethyl benzene into styrene (one of the most important industrial processes).

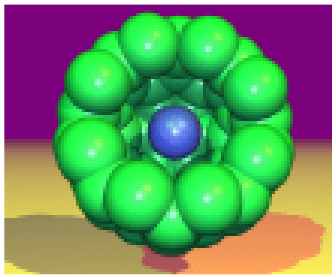
- Interesting electrical properties ➔ data storage, solar cells and fuel cells
- Large non-linear optical response ➔ Suitable for telecommunication applications
- Vesicles made of C_{60} used for drug delivery

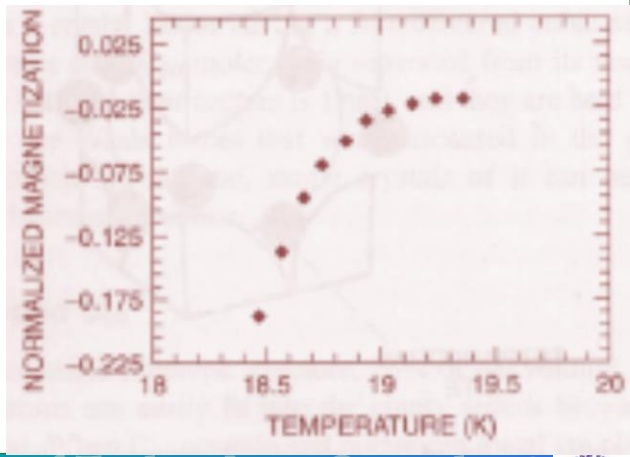
Interesting Properties/Applications of Fullerene

- **Sunscreens ➔ Due to photophysical properties.**
- **Antibacterials ➔ Due to general chemical reactivity**
- **Superconducting materials ➔ Due to physical properties**

Superconducting C_{60} by inserting alkali metals into C_{60}; *e.g.*, $K_3@C_{60}$; K atoms make the crystal electrically conducting. K acts as donor by forming K^+ and C_{60}^{3-}; **T_C at 18.4 K.**

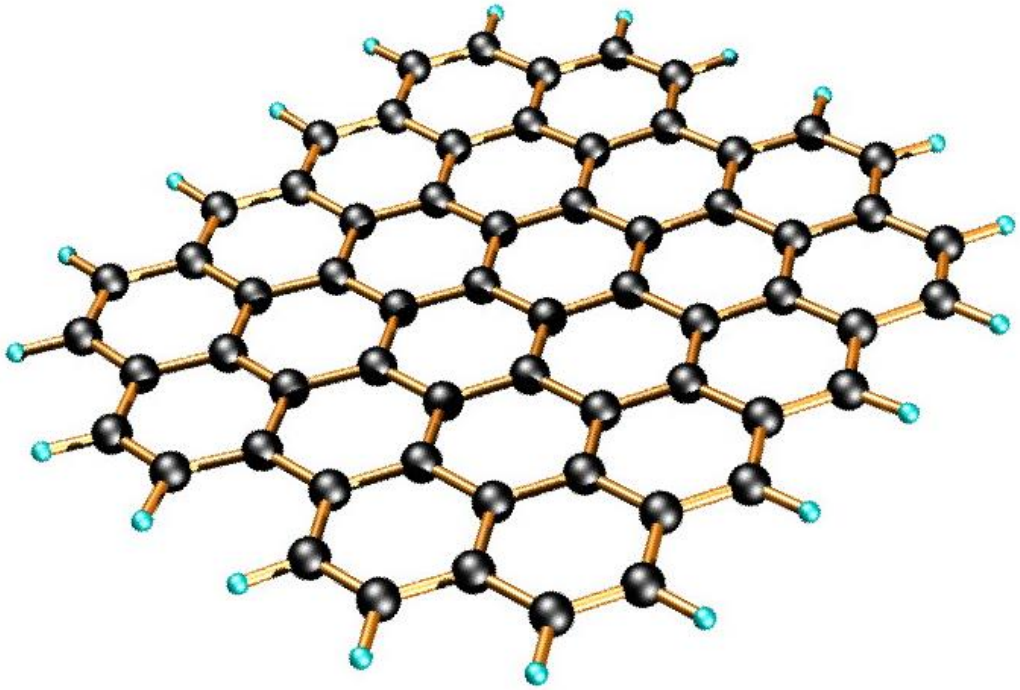
Similarly, Rb-Tl doped C_{60} shows T_C of 45 K!

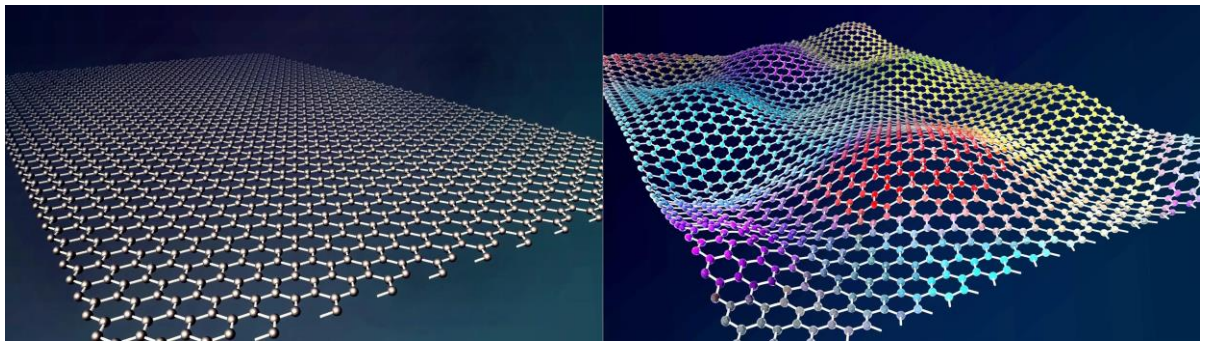




Graphene

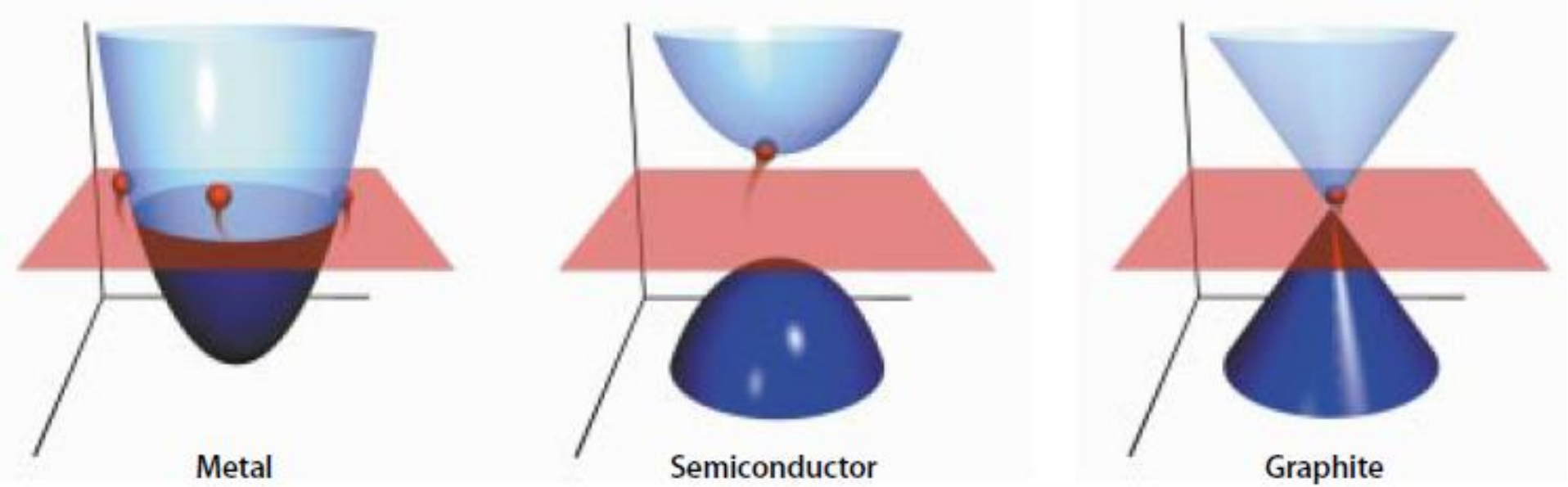
Graphene





- Graphene is an allotrope of carbon in the form of a 2D, atomic-scale, hexagonal lattice in which one atom forms each vertex.
- Graphene has many unusual properties. It is about 200 times stronger than the strongest steel. It efficiently conducts heat and electricity and is nearly transparent. Graphene shows a large and nonlinear diamagnetism.

Electrical properties of Graphene



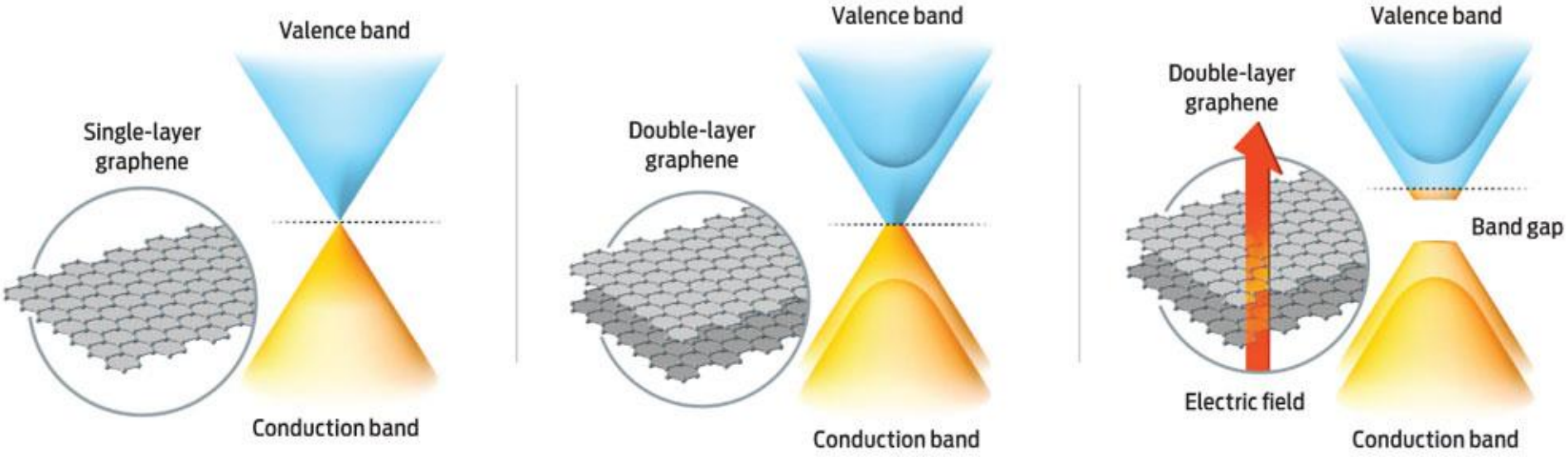
ELECTRICAL PROPERTIES of a material depend on the separation between the energy states that are filled by electrons (*dark blue*) and the "conduction" states that are empty and available for electrons to hop into (*light blue*).

Metals (*left*) conduct electricity easily because there are so many electrons (*red*) with easy access to adjacent conduction states.

In semiconductors (*center*), electrons need an energy boost from light or an electrical field to jump the gap to the first available conduction state.

The form of carbon known as graphite is a semimetal (*right*) that just barely conducts because without these external boosts, only a few electrons can access the narrow path to a conduction state.

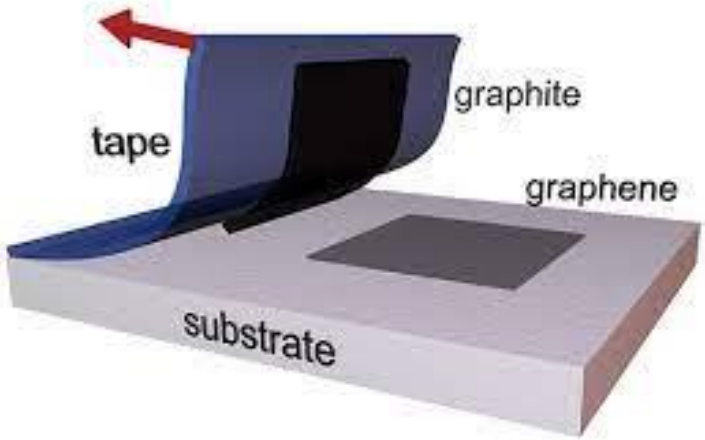
Electrical properties of Graphene

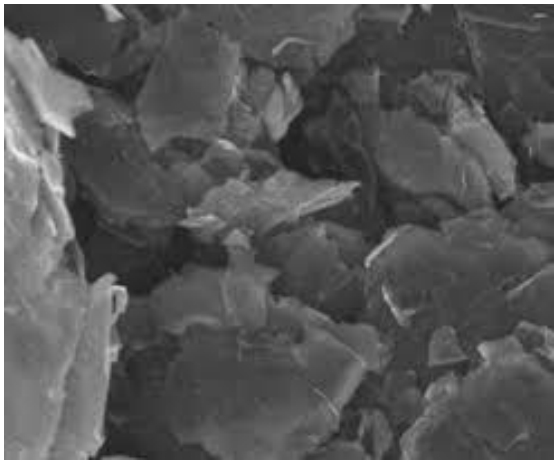


In both single-layer and double-layer graphene [left and middle], the valence and conduction bands are in effect conical and meet at a point, with no band gap.

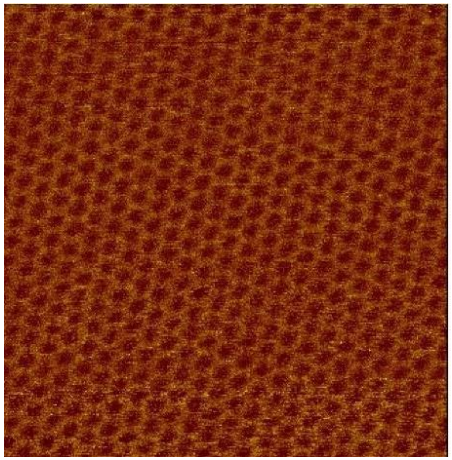
The introduction of an electric field perpendicular to the layers [right] creates an asymmetry, which generates a band gap. Though small, the gap is tunable, creating possibilities for new devices.

Graphene exfoliation

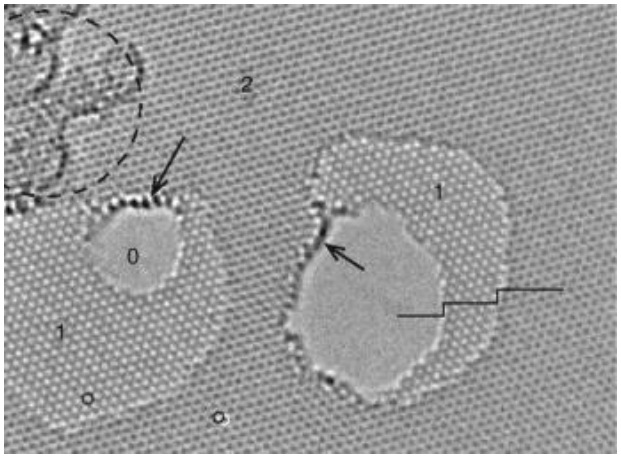




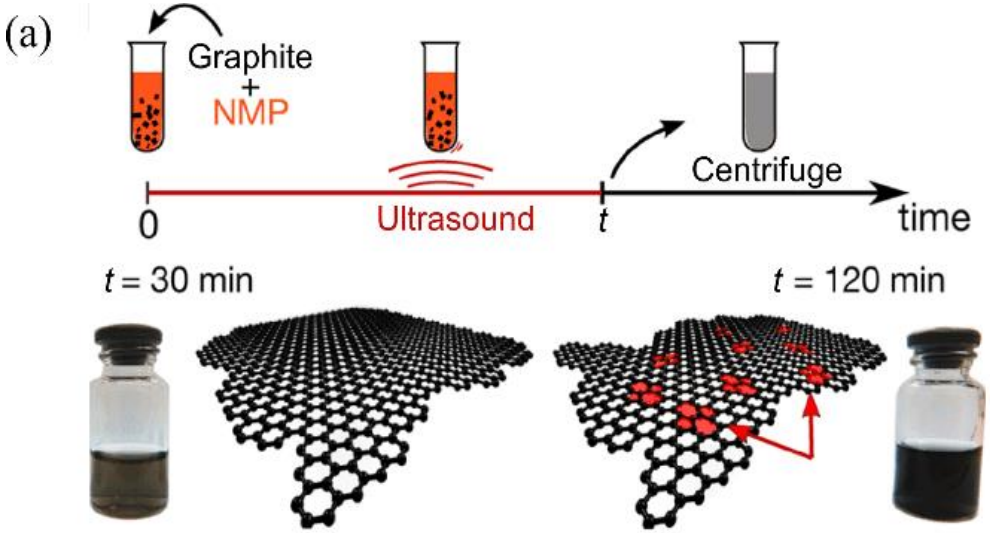
SEM

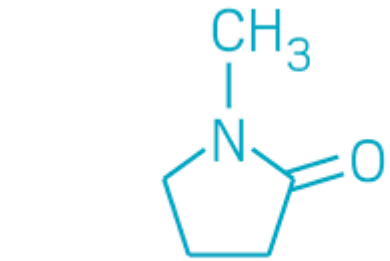


AFM

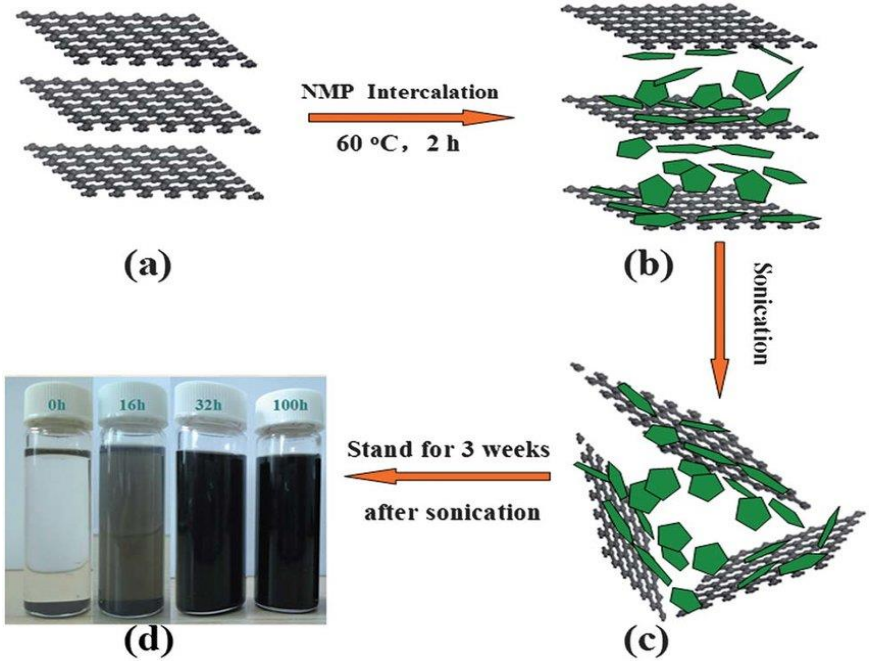


TEM



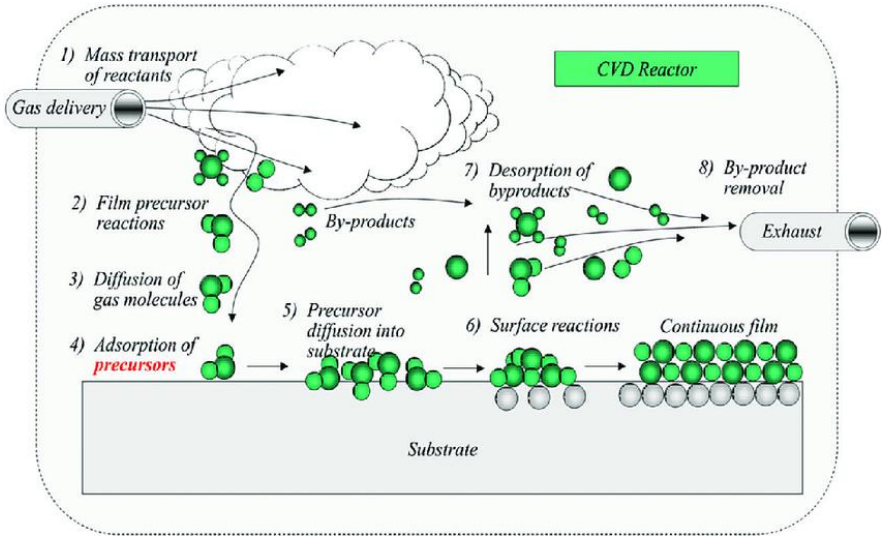


N-methylpyrrolidone



Chemical Vapor Deposition (CVD)

CVD belongs to the "bottom-up" technology. Its principle is to introduce the vapor of gaseous or liquid reactant containing film elements and other gases needed to react into the reaction chamber.



CVD consists of four main stages:

① The reaction gas diffuses to the surface of the material.

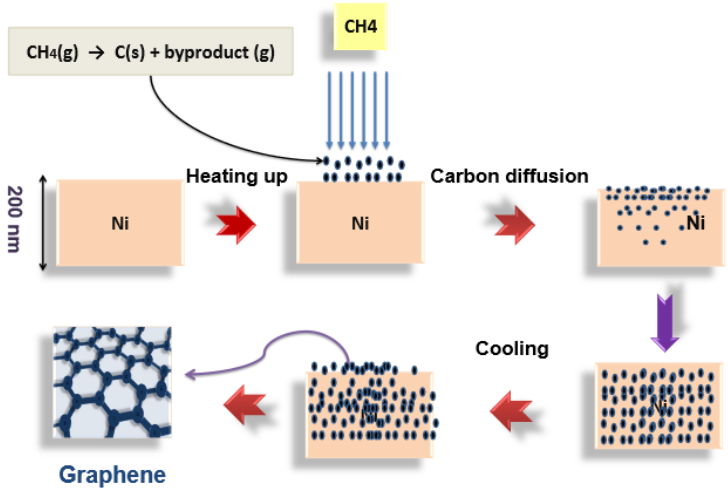
② The reaction gas is adsorbed on the surface of the material.

③ Chemical reaction occurs on the surface of the material.

④ The gaseous by-products are separated from the material surface.

Because of the molecular level nucleation or growth, CVD is more suitable for forming dense and uniform films on the irregular substrate surface. CVD deposition speed is fast, and film quality is stable. Some notable films also have excellent optical, thermal, and electrical properties, making it easy to achieve mass production.

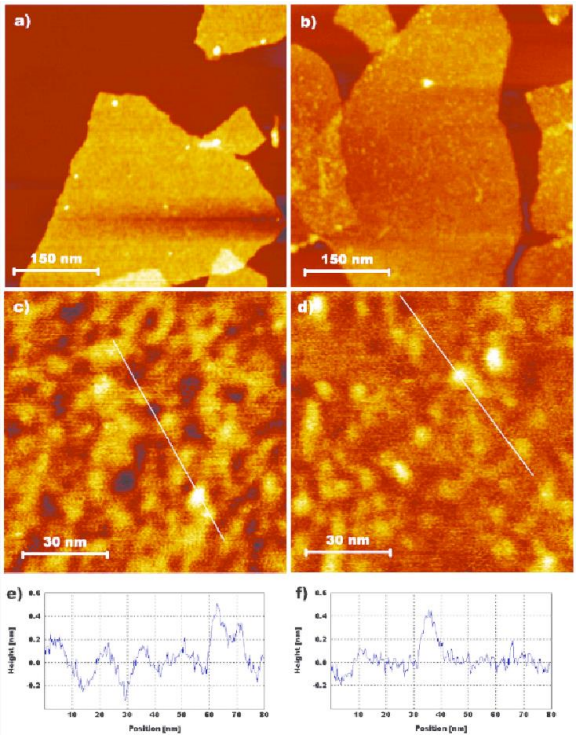
The deposition temperature of CVD is usually very high, between 900 ℃ ~ 2000 ℃.

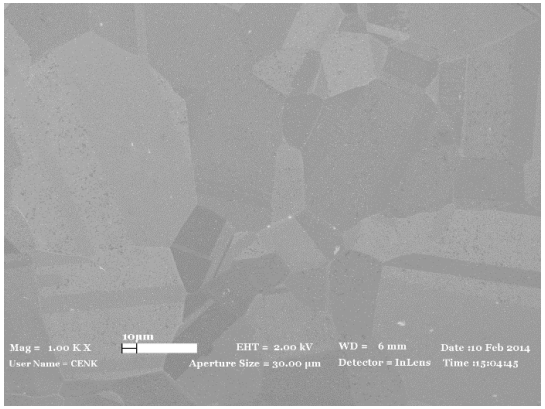


- Substrate temp= 1000 ºC
- Carrier gas= H_2

The CVD process for graphene growth on a nickel foil can be simplified into four elemental steps:

1. adsorption and decomposition of the carbon precursor (for example, methane);
2. diffusion on the surface and dissolution of the decomposed active carbon species into the bulk;
3. segregation of dissolved carbon onto the surface; and
4. subsequent nucleation & growth.



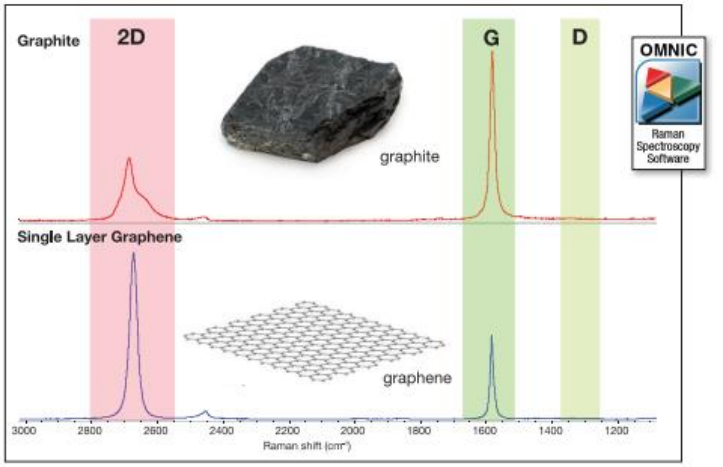


Raman spectroscopy is a fast, nondestructive, and high-resolution tool for the characterization of the lattice structure and the electronic, optical, and phonon properties of carbon materials, including three-dimensional (3d) diamond and graphite, 2d **graphene**, 1d carbon nanotubes, and 0d fullerenes.

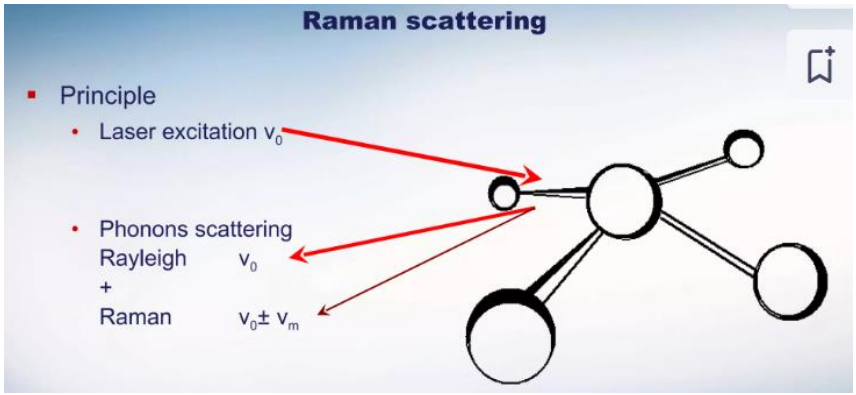
Monolayer Graphene

Bilayer graphene

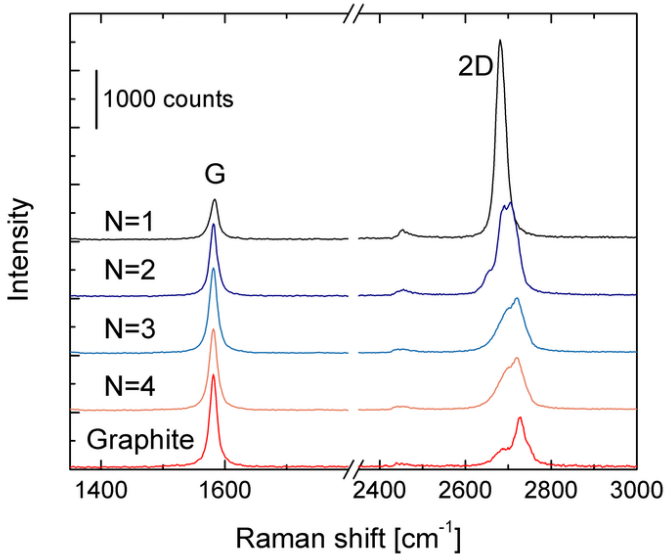
Trilayer graphene

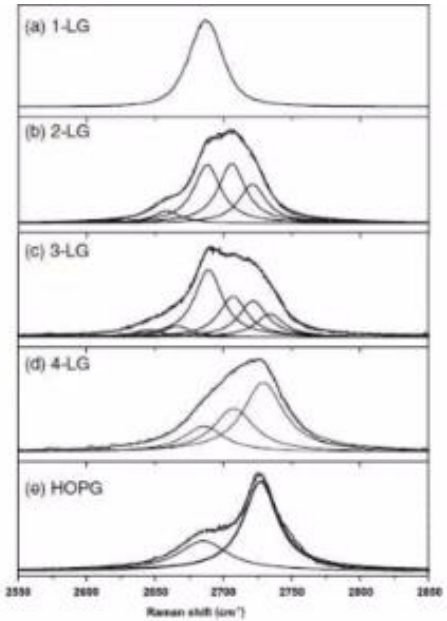


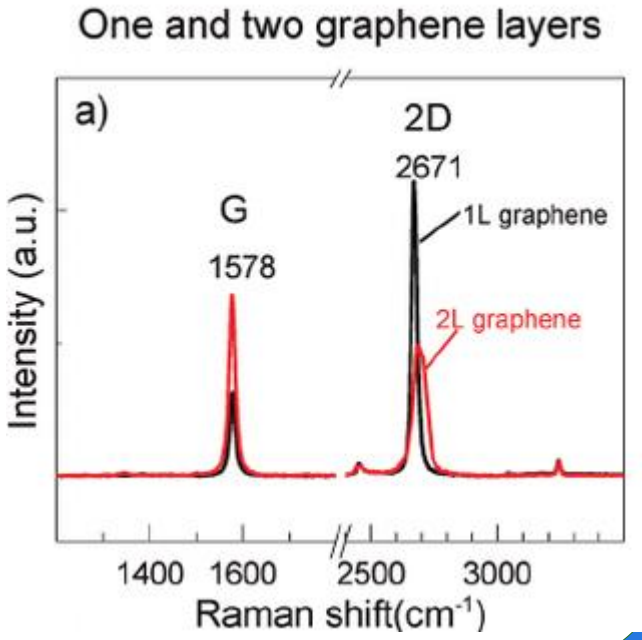
- Raman spectroscopy is a vibrational technique that is extremely sensitive to geometric structure and bonding within molecules.
- Even small differences in geometric structure lead to significant differences in the observed Raman spectrum of a molecule.
- This sensitivity to geometric structure is extremely useful for the study of the different allotropes of carbon (i.e. diamond, carbon nanotubes, buckminster fullerenes, carbon nanoribbons, etc.).

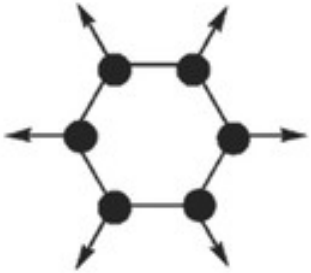


- The G band is a sharp band that appears around 1587 cm^{-1} in the spectrum of graphene. The band is an in-plane vibrational mode involving the sp^2 hybridized carbon atoms that comprises the graphene sheet.
- The G band position is highly sensitive to the number of layers present in the sample and is one method for determining layer thickness and is based upon the observed position of this band for a particular sample.
- The D band is known as the disorder band or the defect band and it represents a ring breathing mode from sp^2 carbon rings, although to be active the ring must be adjacent to a graphene edge or a defect.
- The D band band is typically very weak in graphite and is typically weak in high quality graphene as well.
- If the D band is significant it means that there are a lot of defects in the material.
- The 2D band is the second order of the D band, sometimes referred to as an overtone of the D band.
- The 2D band band is also used to determine graphene layer thickness. The 2D band method depends not only on band position but also on band shape.

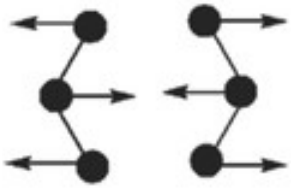






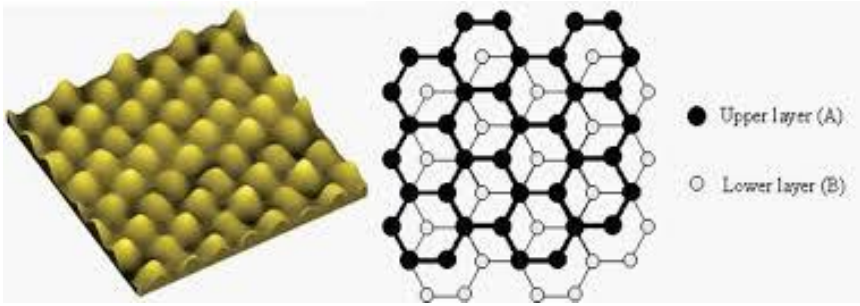


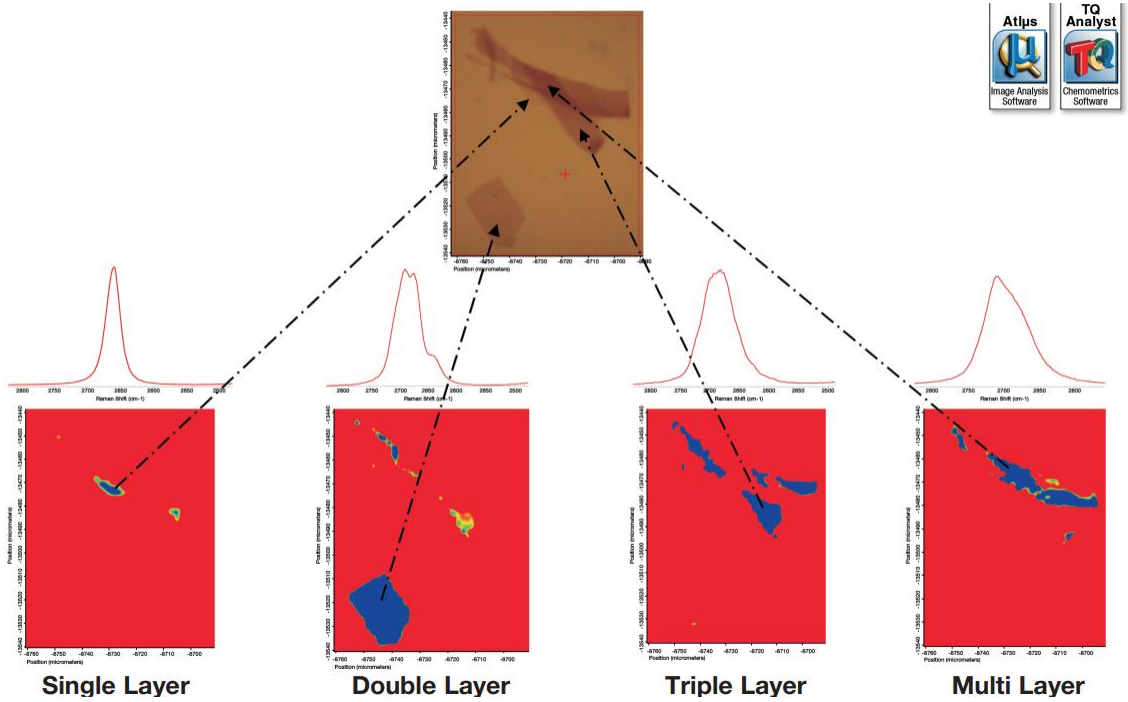
D mode (breathing A_{1g})



G mode (E_{2g})

HOPG





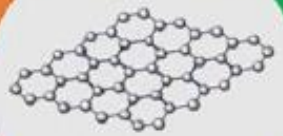
Applications of Graphene

- Solar cell
- Fuel cell
- Batteries
- Supercapacitors

Energy

Environment

- Environment treatment and protection
- Desalination technologies



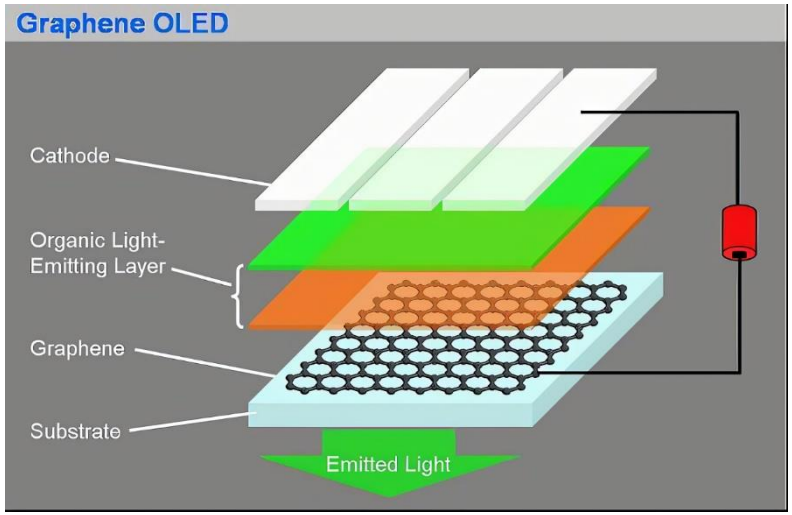
Graphene

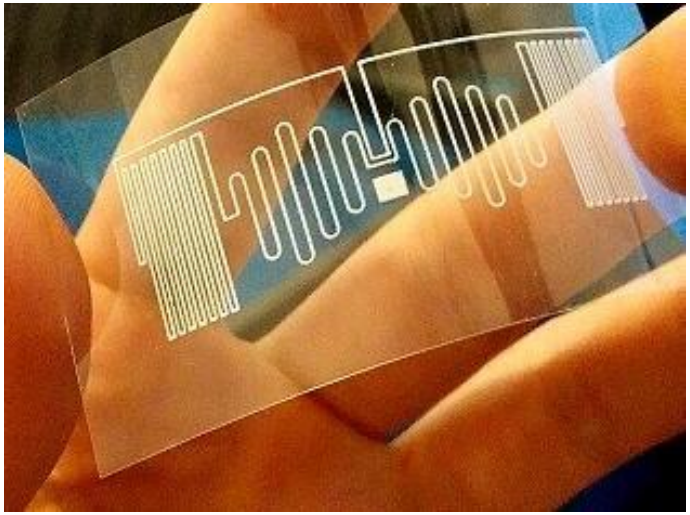
Sensor, bio-sensor and heat-sink

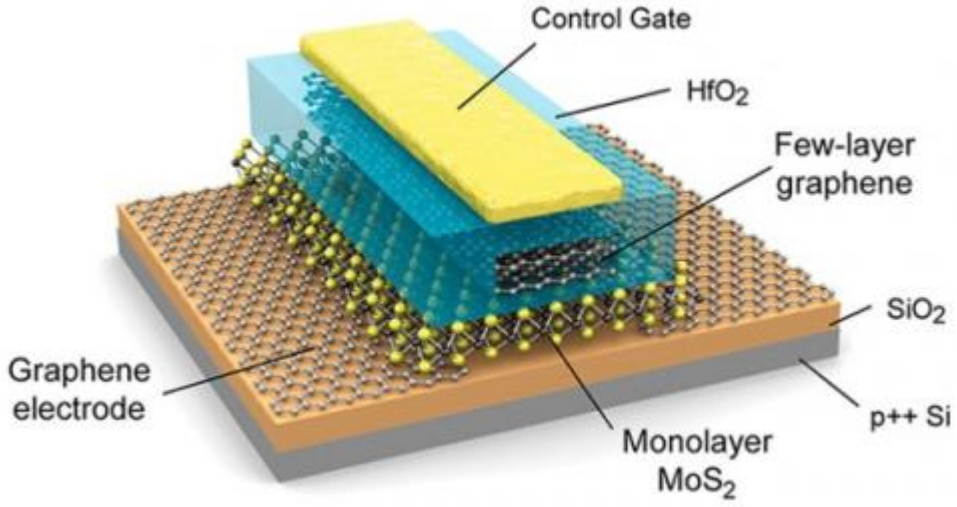
- Sensor and biosensor
- Semiconductor
- Composite
- Flexible and transparent material
- Ink conductive
- Electronic device

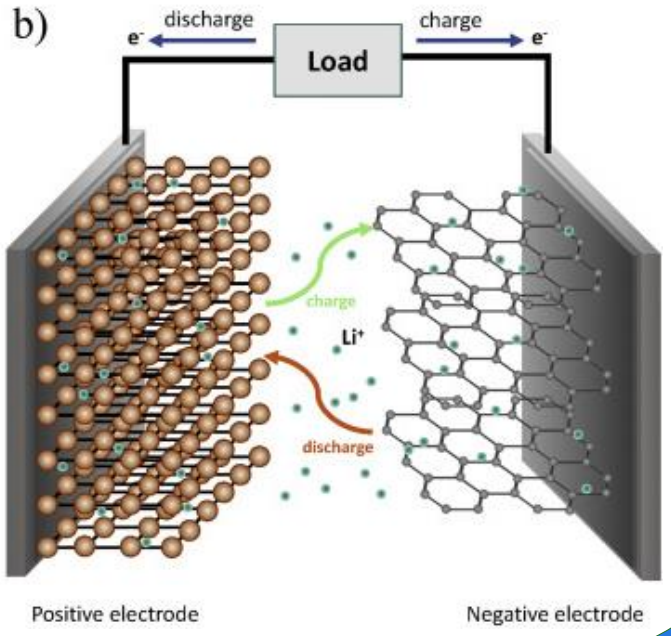
Biomedical

- Diagnostic technology
- Drug delivery
- Therapy technology
- Scaffolds material


Graphene OLED
Cathode
Organic Light-Emitting Layer
Graphene
Substrate
Emitted Light



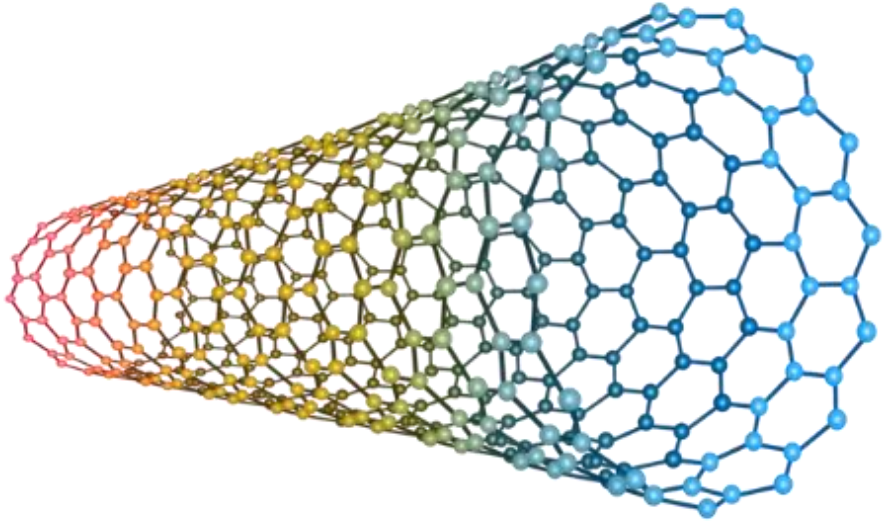

Control Gate
HfO_2
Few-layer graphene
SiO_2
Graphene electrode
p++ Si
Monolayer MoS_2

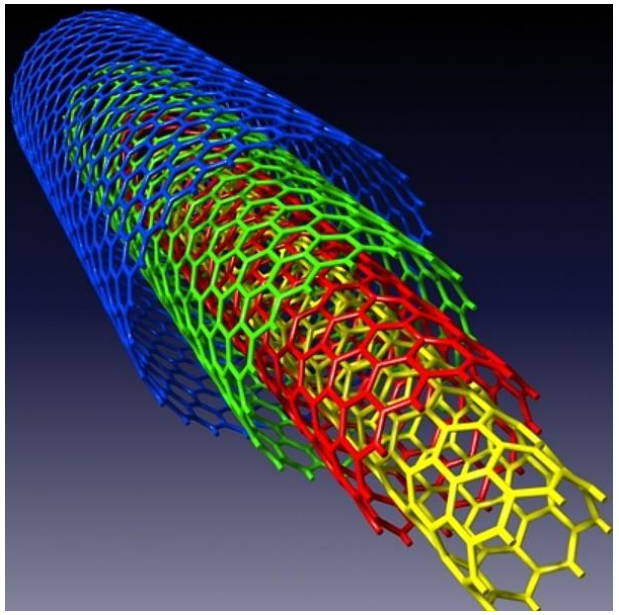

b)
discharge
charge
e⁻
e⁻
Load
charge
Li⁺
discharge
Positive electrode
Negative electrode

Carbon Nanotubes

Carbon Nanotube Moving into Cylindrical

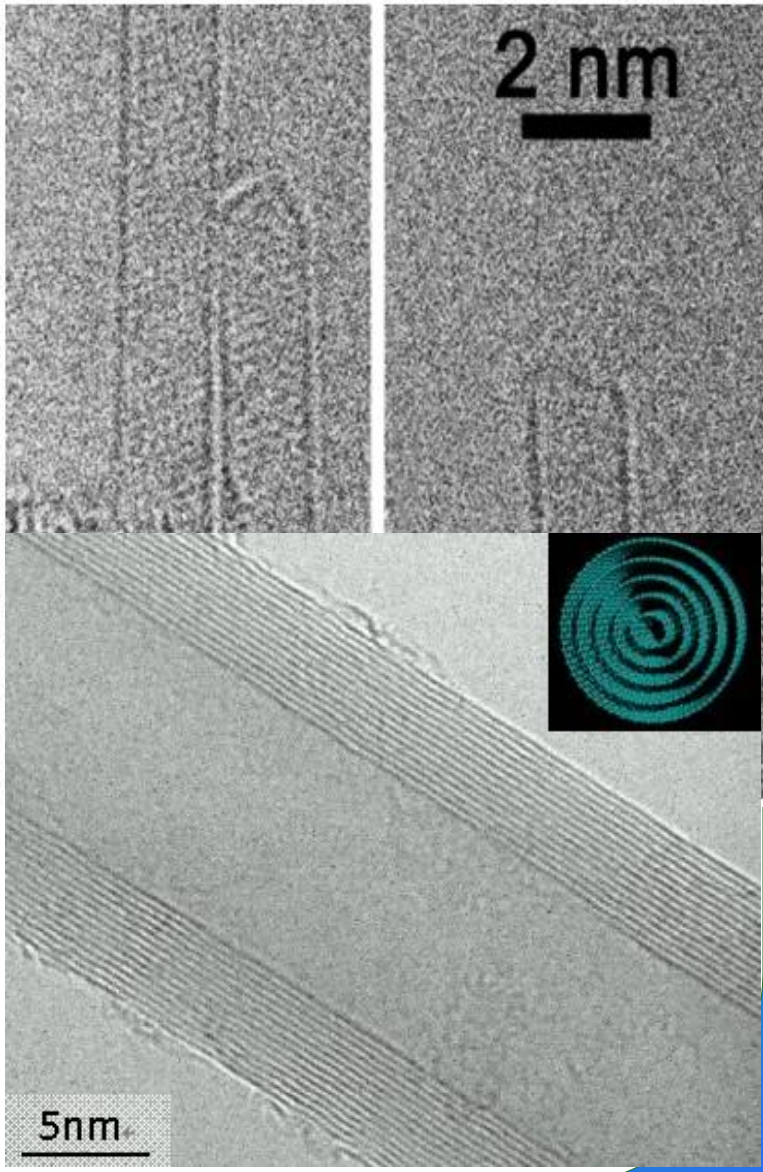
- **Cylindrical fullerene was discovered in 1991 by S Iijima (*S. Iijima, Nature, **354*** (1991) *56.*)**
- **Internal cylinder diameter of 1 to 50 nm**
- **Length of about 100 nm up to several micrometers and longer**
- **Formed as Single-walled (SWCNTs) and Multi-walled (MWCNTs)**
- **Semiconducting in nature**



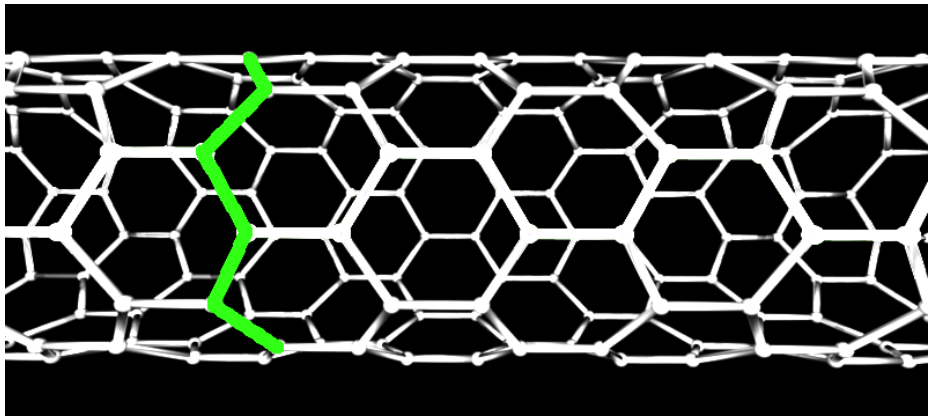


Carbon Nanotube: Characteristics

- Long, hollow structure with the walls formed by one-atom-thick sheets of carbon, called graphene. Take a sheet of graphene of finite width *W* and wrap it into a cylinder of fixed radius *R* and arbitrary length.
- Sheets are rolled at specific and discrete angles. Properties change accordingly.
- Combination of rolling angle and radius decides the nanotube properties as semiconductor or metals.
- The chemical bonding is composed entirely of sp^2 bond.
- Individual nanotubes naturally align themselves into ropes held together by van der Waals forces.

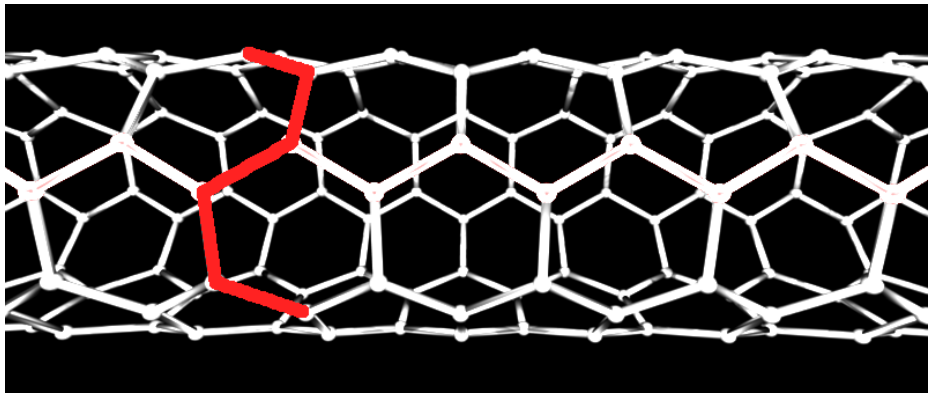


Zig-zag Carbon Nanotube



A zigzag path on a graphene-like lattice as a path that turns 60 degrees, alternating left and right, after stepping through each bond.

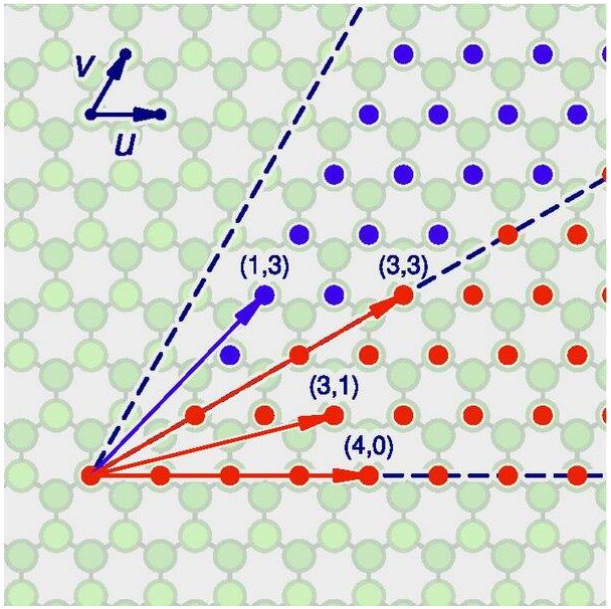
Arm chair Carbon Nanotube

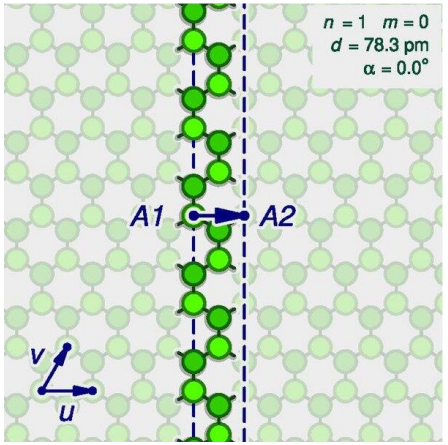


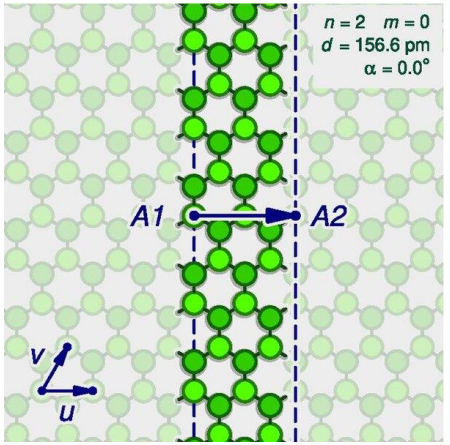
If the tube is instead encircled by a closed armchair path.

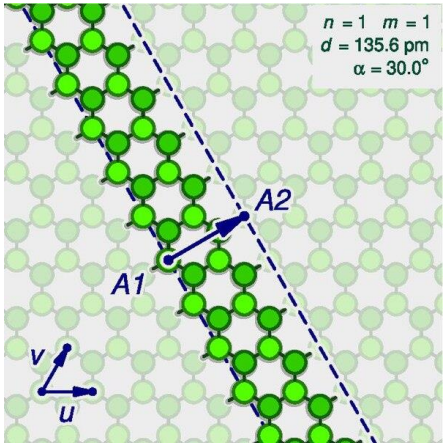
Carbon Nanotube Structure

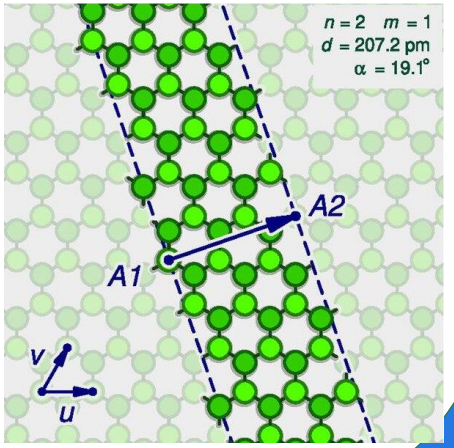
A general infinitely long tube, one should imagine it being sliced open by a cut parallel to its axis, that goes through some atom, and then unrolled flat on the plane, so that its atoms and bonds coincide with those of an imaginary graphene sheet.



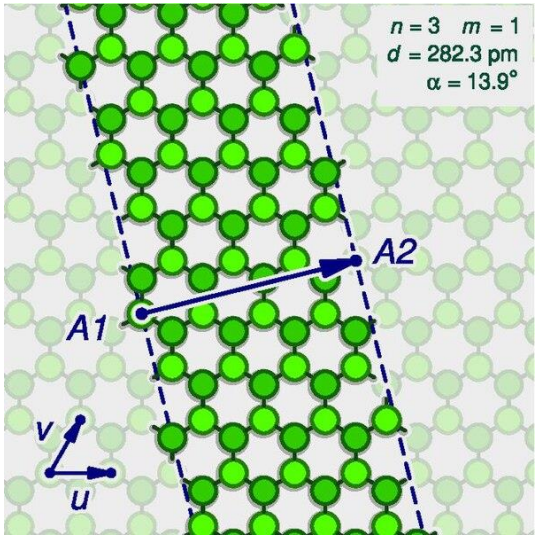


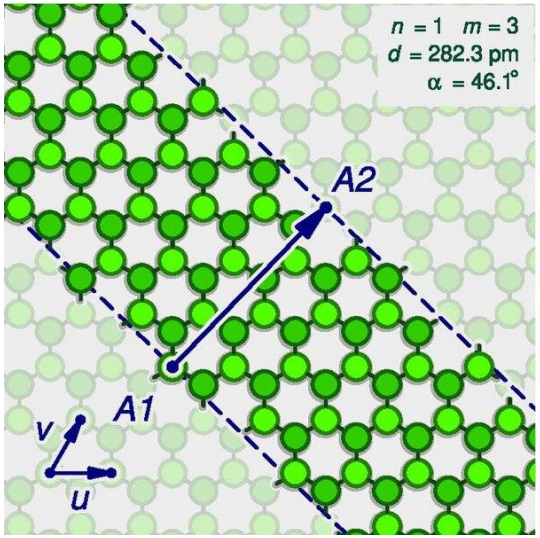


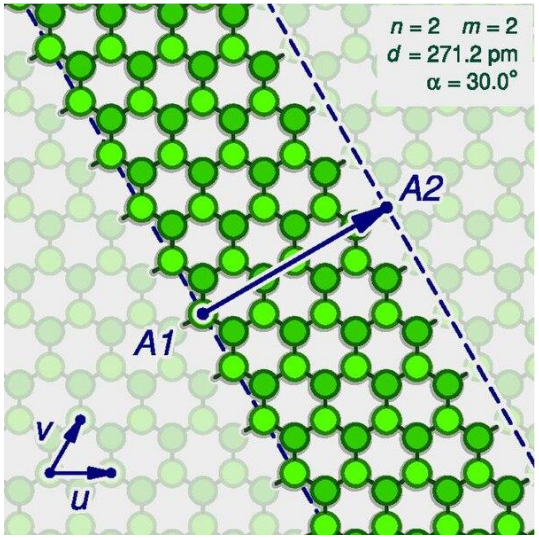




- u and v be two linearly independent vectors.
- The (n, m) pairs that define non-isomorphic carbon nanotube structures (red dots).
- The pairs that define the enantiomers of the chiral ones (blue dots).







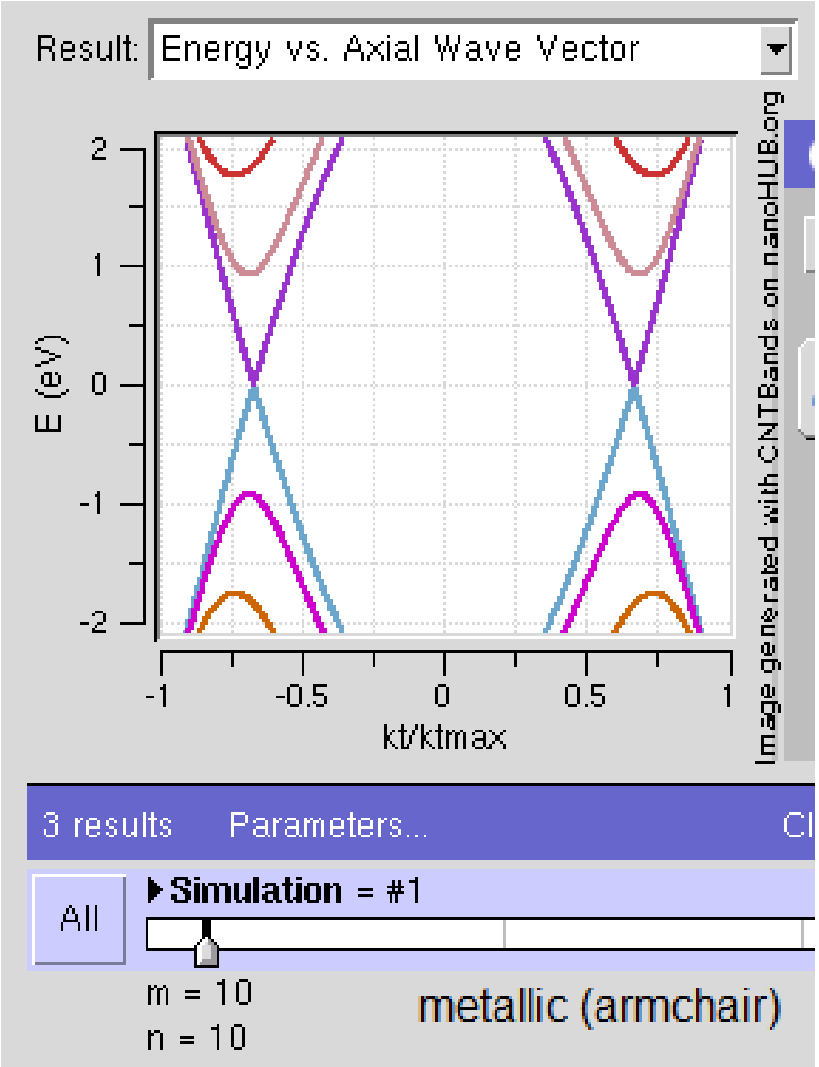
In pm, The diameter (d) of the nanotube $d \approx 78.3\sqrt{((n+m)^2 - nm)}$

The thinnest carbon nanotube proper is the armchair structure with type (2,2), which has a diameter of 0.3 nm.

The observation of the longest carbon nanotubes grown so far, around 0.5 meter long

Electrical properties of straight SWCNT

Graphite is a semimetal (as far as the band structure is concerned).



Properties of SWCNT

Size: 0.6 to 1.8 nm in diameter

Density: 1.33 to 1.40 g/cc (Density of Al is 2.7 g/cc)

Tensile strength: 45 billion Pa (H.S.Steel breaks at ~ 2 billion Pa)

Resilience: Can bend at large angles (metals fracture at grain bound.)

Current carrying cap.: 1 billion Acm^{-2} (Cu burns at ~ 1 million Acm^{-2})

Heat transmission: ~6000 W/m.K at RT (Diamond 3320 W/m.K)

Temperature stability: stable to 2800° C in vacuum and 750° C in air

(metal wires in μchips melt at 600° to 1000 °C)

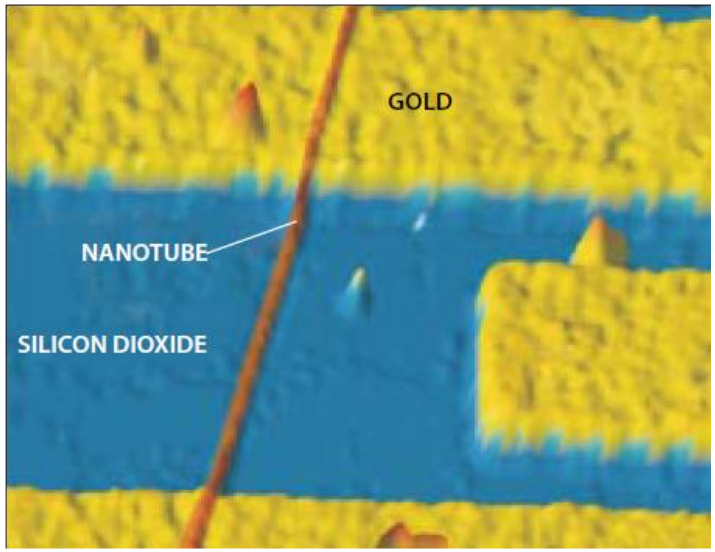
Field emission: Activate phosphors at 1-3 V if electrodes are at 1 μm

(Mo tips require 50 to 100 V/μm + limited life time)

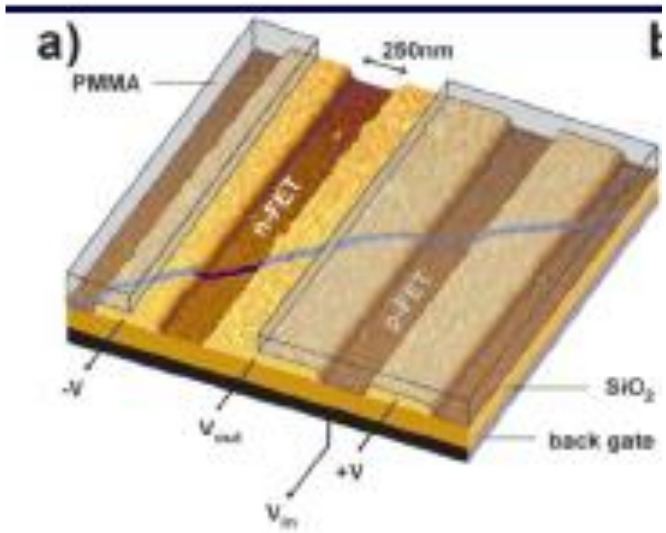
Cost: US$ 1,500 per g (Gold is selling at ~ $15 per g)

Applications of CNT

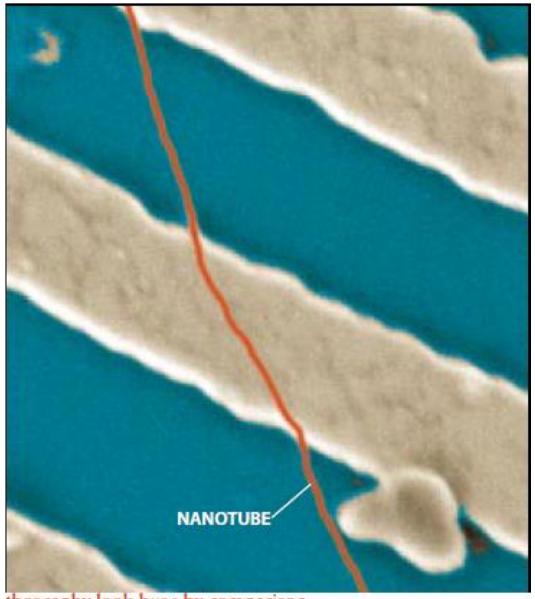
Main: Electrical



← SW →



MICROCHIPS OF THE FUTURE will require smaller wires and transistors than photolithography can produce today. Electrically conductive macromolecules of carbon that self-assemble into tubes (*top left*) are being tested as ultrafine wires (*left*) and as channels in experimental field-effect transistors (*above*).



thography look huge by comparison.

Chemical and genetic probes: *Tagged strand of DNA*: CNT-tipped AFM can trace a strand of DNA and identify chemical markers of gene variants (Demonstrated).

Mechanical memory: *Nonvolatile RAM*: Screen of CNT tested as binary memory device (speed ~ 1 MHz) (Demonstrated).

Nanotweezers: *Pincers 5 μm long*: Two CNTs attached to electrodes on glass could move 500 nm objects (sticky!) (Demonstrated).

Supersensitive sensor: *Oxygen sticks to CNT*: Electrical resistance changes dramatically when exposed to alkali, halogens and other gases at RT (distinguishability!) (Demonstrated)

Hydrogen & Ion storage: *Atoms in core*: Can store hydrogen (and lithium) later release it (only 6.5% hydrogen in-take) (under test).

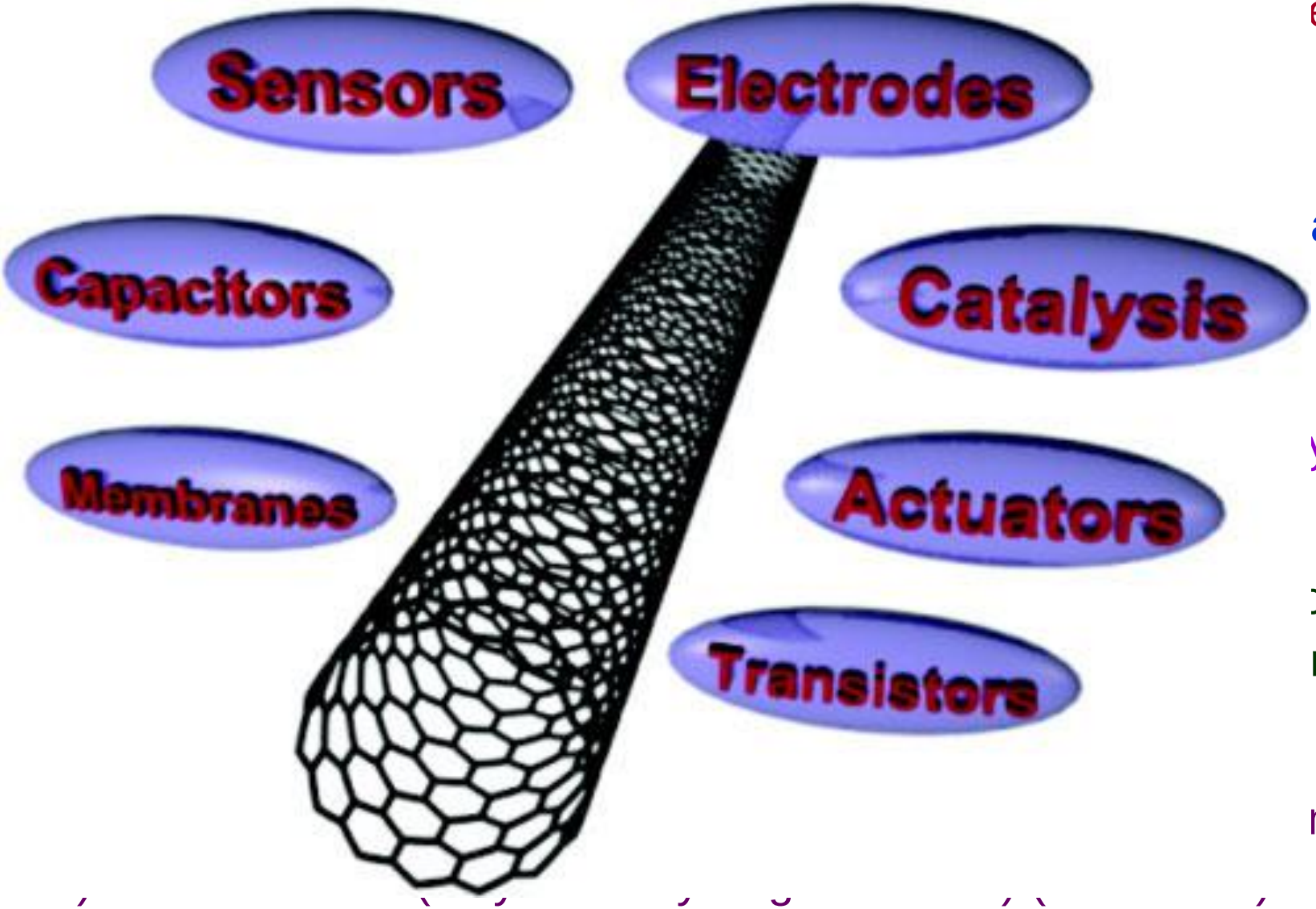
Ch ed
AF of
ge

Me as
bin

Na to
ele y!)
(D

Su cal
res ns
an

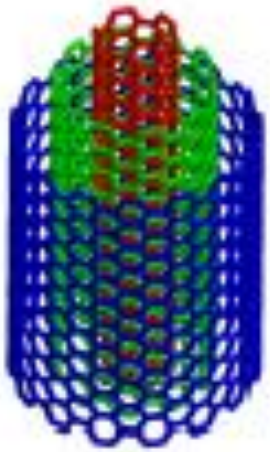
Hy nd
lith



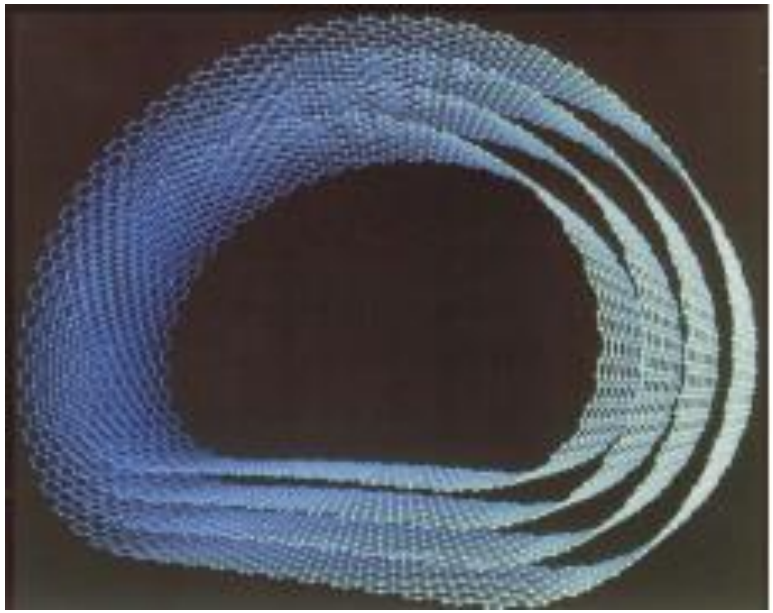
Multi-walled Carbon Nanotube

- Each part of MWCNT tube is made of SWCNT, with same kind of structure and chirality.
- Nested inside each other with interlayer separation of ~ 3.4 Å, just as in graphene.
- Interlayer interaction is weak (vdW).

- Chirality of individual tubes need not be correlated.
- Easy to manufacture.
- SW and MW CNTs may be open ended or “capped” with fullerene-like gaps.
- Capped tubes are more stable, but less interesting.



Electrical properties of MWCNT



MWCNT's bandgap is proportional to 1/d at room temperature

MWCNT behave like metals since *d* ~10 nm

Only the outer most shell carries current in a MWCNT.

Max. current density: > 5×10^{13} Am^{-2} (For a supercond. $J_C \sim 10^{12}$ Am^{-2})

Resolution

For a microscope, the limit of resolution is given by

$$x = \frac{\lambda}{2A}$$

where λ is the wavelength of light used, and A is the numerical aperture.

Hence, substituting the values, $x = \frac{600}{2 \times 0.12}$

which gives, $x = 2.5\ \mu m$

Scanned with CamScanner

Aperture refers to the opening of a lens's diaphragm through which light passes.

Energy of electron, E = 10 KeV

$$= 10 \times 10^3 \text{ eV}$$

$$E = 10^4 \times 1.6 \times 10^{-19} J = \frac{1}{2} m_e V^2$$

$$\frac{1}{2}(m_e v^2) \times \frac{m_e}{m_e} = E$$

$$\frac{(m_e V)^2}{2m_e} = E$$

$$m_e v = \sqrt{2 m_e E}$$

$$= \sqrt{2 \times 9.11 \times 10^{-31} \times 1.6 \times 10^{-15}}$$

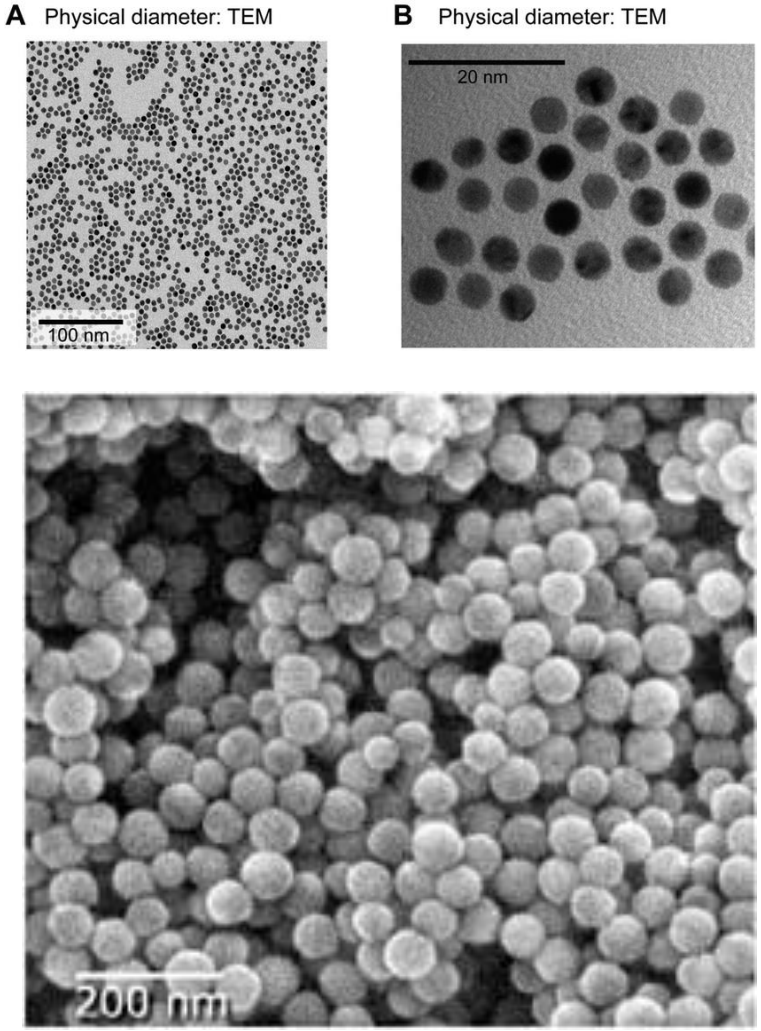
Momentum, $p = m_e v = 5.4 \times 10^{-24}$

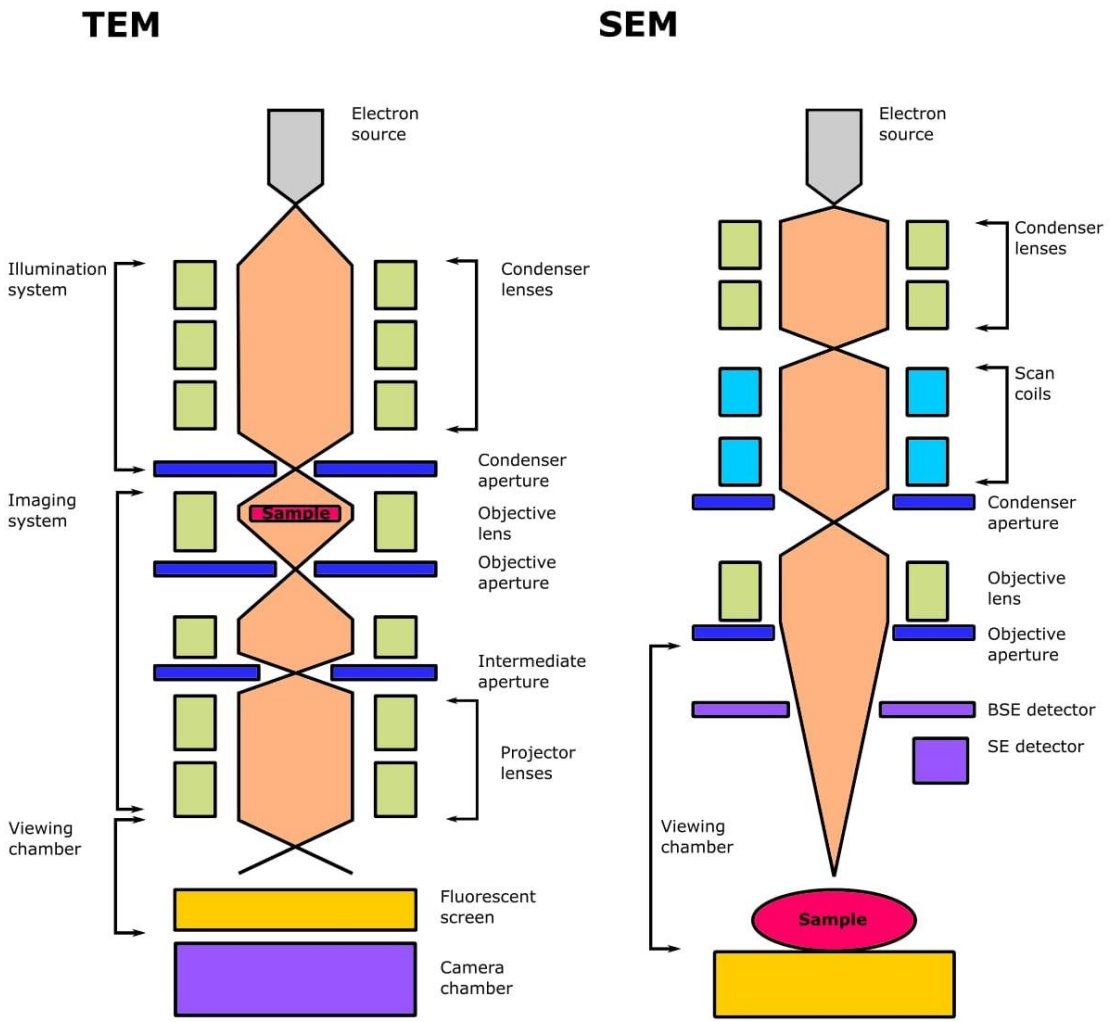
De-Broglie wavelength, $\lambda = \frac{h}{p} = \frac{6.626 \times 10^{-34}}{5.4 \times 10^{-24}}$

$$\lambda = 1.227 \times 10^{-11} m$$

$$= 0.1227 \times 10^{-10} \text{ m}$$

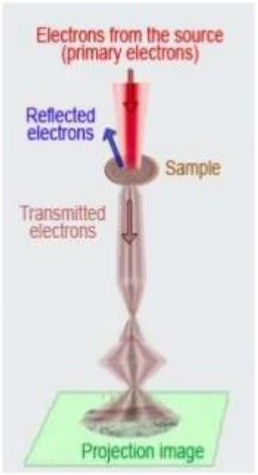
$\boxed{\lambda = 0.1227 Å}$


A Physical diameter: TEM
100 nm
B Physical diameter: TEM
20 nm
200 nm


TEM
SEM
Electron source
Illumination system
Condenser lenses
Condenser aperture
Imaging system
Sample
Objective lens
Objective aperture
Intermediate aperture
Projector lenses
Viewing chamber
Fluorescent screen
Camera chamber
Electron source
Condenser lenses
Scan coils
Condenser aperture
Objective lens
Objective aperture
BSE detector
SE detector
Viewing chamber
Sample

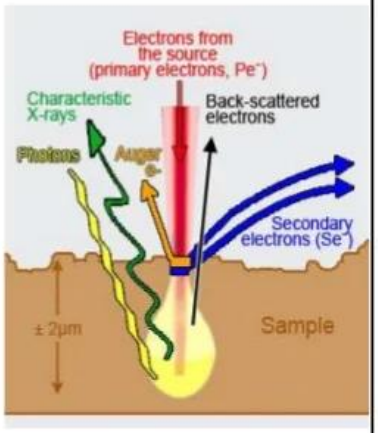
PRINCIPLE OF WORKING OF TEM

- Electrons possess a wave like character.
- Electrons emitted into vacuum from a heated filament with increased accelerating potential will have small wavelength.
- Such higher-energy electrons can penetrate distances of several microns into a solid.
- If these transmitted electrons could be focused - images with much better resolution.
- Focusing relies on the fact that, electrons also behave as negatively charged particles and are therefore deflected by electric or magnetic fields.



PRINCIPLE OF WORKING OF SEM

- Incoming (primary) electrons
  - can be "reflected" (backscattered) from a bulk specimen.
  - can release secondary electrons.
- Primary electrons are focused into a small-diameter electron probe that is scanned across the specimen.
- Electrostatic or magnetic fields, applied at right angles to the beam, can be used to change its direction of travel.
- By scanning simultaneously in two perpendicular directions, a square or rectangular area of specimen (known as a **raster**) can be covered.
- Image of this area can be formed by collecting secondary electrons from each point on the specimen.



Scanning Electron Microscope (SEM)

Secondary electrons, however, originate from the atoms of the sample. They are a result of inelastic interactions between the electron beam and the sample.

100–300 kV accelerating voltage is suitable for TEM specimens.

The accelerating voltage of a scanning electron microscope is variable, usually in the range 500-30,000 volts

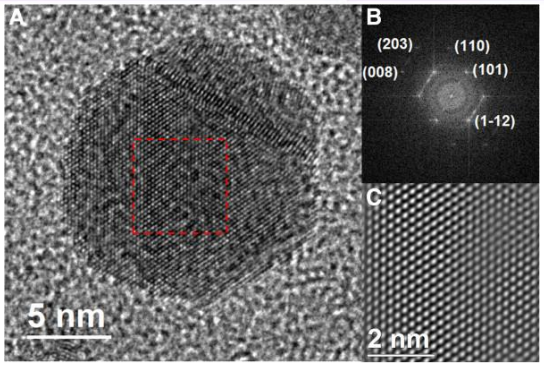
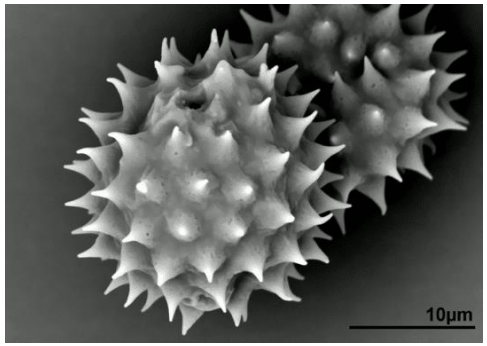
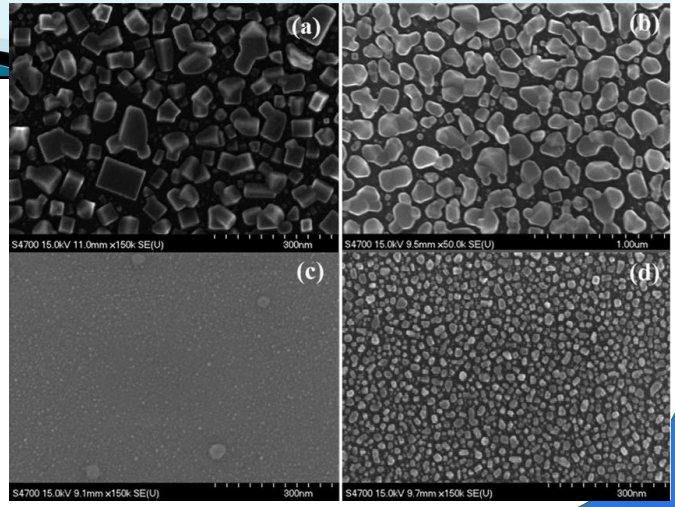
SEM V/S TEM

SEM	TEM
• in SEM is based on scattered electrons	• TEM is based on transmitted electrons
• The scattered electrons in SEM produced the image of the sample after the microscope collects and counts the scattered electrons.	• In TEM, electrons are directly pointed toward the sample.
• SEM focuses on the sample's surface and its composition.	• TEM seeks to see what is inside or beyond the surface.
• SEM shows the sample bit by bit	• TEM shows the sample as a whole.
• SEM provides a three-dimensional image	• TEM delivers a two-dimensional picture.
• SEM only offers 2 million as a maximum level of magnification.	• TEM has up to a 50 million magnification
• SEM has 0.4 nanometers.	• The resolution of TEM is 0.5 angstroms

Differences between TEM and SEM

Transmission electron microscope

- It is used to observe finer details of internal structures.
- Uses electromagnetic coils and high voltages.
- Electrons beams are passing through the specimen
- Flat images produced by TEMs

Scanning electron microscope

- This microscope is used to observe the surface structure of microscopic objects.
- Uses low voltages
- Instead of traveling through the specimen, the electron beam effectively bounces straight off it.
- Are generally about 10 times less powerful than TEMs
- Produce very sharp, 3D images